

FREYDLEIN, R. A.

Synthesis of *α*-amino-*β*-hydroxy acids starting with *α,α*-dichloro-*α*-keto acids: A. N. Nosov, V. I. Kuznetsov, L. I. Zhegerlein, B. I. Vassilov, V. A. Kozlov, and T. T. Vasil'eva (Inst. Higher Chemical Compounds, Moscow). *Zhur. Obshch. Khim.* 27, 2418-22 (1953); cf. C.A. 50, 4849f. —Heating 80 g. *β*-chloro-*α*-valeric acid and 40 ml. liquid NH₃ in an autoclave 10 hrs. at 250° gave 93% *α*-*β*-lactones, b_p 128-30°, m. 39-40°. Similarly NH₃ and Rt *β*-chloro-*α*-valeric acid at 120-40° in 3 hrs. gave 65% yield. Identifying *α*-chloro-*α*-anthanic acid with 25% NH₄OH 2 hrs. at 100° gave after passage of the mixt. through a cationic resin, washing the latter with H₂O and eluting with 6% NH₄OH gave 10% l-aminododecanic acid and 72% *α*-aminocyclohexanecarboxylic acid, m. 184-5°; HCl salt, m. 99-100°. Similarly *α*-chloro-*α*-nonanoic acid and 25% NH₄OH for 1 hr. at 100° gave 82.6% *α*-aminononanoic acid, m. 160-60°; 11-chloro-undecanoic acid gave after 48 hrs. in 40% NH₄OH at room temp. 11-aminoundecanoic acid, m. 185-6°. Reaction of 32.8 g. 1,1-dichloro-5-cyano-1-pentene with 210 ml. *N* LiAlH₄ in Et₂O gave 91% 1,1-dichloro-6-amino-1-hexene, b_p 81-2°, n_D²⁰ 1.4938, d₄²⁰ 1.1338 (*N*-phthaloyl deriv., m. 57-8°); similarly was prepd. 91% 1,1-dichloro-8-amino-1-octene, b_p 72°, 1.4240, 1.0765 (*N*-phthaloyl deriv., m. 61-2°). The latter (35 g.) added to 200 g. H₂SO₄ (d. 1.82) and warmed 0.5 hr. at 60-8° gave after pouring on ice and partial neutralization Dist. 4843/4E2c(1)/4E3d

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AN. Nesmeyanov, R.Kh. Fabelina

with BaO, completed with NH₄OH, gave after passage over ion-exchanger as above, 85% 8-aminodecanoic acid, m. 102-2.5°. To 320 g. 1,1,1,0-tetrachlorononane was added at 80° 20 ml. SbCl₅ and after final heating to 100° the mxt. was taken up in CHCl₃ and washed with aq. HCl yielding 82% 1,1,1-trichloro-1-nonene, b.p. 82°, 1.4830, 1.1334, which (65 g.) heated with 20.5 g. NaCl in 50 ml. H₂O and 200 ml. Methyl Cellosolve 12 hrs. at 120°, freed of solvent and dild. with H₂O gave 90% 1,1-dichloro-8-cyano-1-nonene, b.p. 122-8°, 1.4777, 1.0584, which with LiAlH₄ as above gave 87% 1,1-dichloro-10-amino-1-decane, b.p. 97-8°, 1.4820, 1.0425. This in H₂SO₄ as above in 45 min. at 70° gave 84% 10-aminodecanoic acid, m. 189.5-90°. G. M. Kosolapoff

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FREYDLINA, R.K.

Thermal telomerization of methylchlorosilanes with C_4H_8
 102. A. N. Nigmatov, R. Kh. Freydlina, and E. Ts.
 Chukovskaya (Inst. Hetero-Org. Compds., Acad. Sci.
 U.S.S.R., Moscow). *Doklady Akad. Nauk S.S.S.R.* 112, 271-2 (1957).—Heating 123 g. MeSiHCl_2 2 hrs. in a steel
 autoclave with C_4H_8 to 260° and a final pressure of 60 atm.
 gave 89% conversion to telomerization products MeSiCl_2
 $(\text{CH}_2\text{CH}_2)_n\text{H}$, with $n = 1-6$, as follows (n, % yield, b.p.,
 n_D^{20} , and d_4^{20} shown): 1, 23.0, b. 100°, —, 2, 25.6, b.
 147-8°, 1.4312, 1.0427; 3, 17.7, b. 91°, 1.4340, 0.9331;
 4, 13.4, b. 64°, 1.4440, 0.9701; 5, 6.7, b. 111-14°, 1.4490,
 0.9600; 6, 3.3, b. 124-7°, 1.4532, 0.9502. About 5.5%
 undescribed higher telomers were also formed. A similar
 reaction of MeSiHCl_2 and C_4H_8 was run 3 hrs. at 280-75°
 and 100 atm. max. pressure yielded from 151 g. MeSiHCl_2 ,
 216 g. products giving $\text{MeSiCl}_2(\text{C}_2\text{H}_5)_n\text{H}$ (n shown) as
 follows: 1, 49, b. 123-4°, 1.4240, —; 2, 26.2, b. 82°,
 1.4400, —; 3, 8.9, b. 89-2°, 1.4510, —; 10% undescribed
 higher telomers. G. M. Kozlovskii.

FREYDLINA, R.Kh.

AUTHOR NESMEYANOV A.N., Member of the Academy of Science, PA - 2916
 FREIDLINA R.Kh., CHUKOVSKAYA E.Ts.,
 TITLE Thermal Telomerization of Trichlorsilane With ethylene.
 (Termicheskaya telomerizatsiya trikhlorosilana s etilenom -Russian)
 PERIODICAL Doklady Akademii Nauk SSSR, 1957, Vol 113, Nr 1, pp 120-122, (U.S.S.R.)
 Received 6/1957 Reviewed 7/1957
 ABSTRACT The silicon compounds containing a Si-H-binding are able to bind themselves to a double or triple binding of many organic compounds. In a former paper we gave a survey of such reactions. Recently, an affiliation of trichlorsilane to a double-binding of acronitrile, 2-vinylpyridinium and allylzyanide was described and an ion mechanism for these reactions was suggested. Nozakura showed that tetrapyridinium nickel chloride catalyzes the affiliation of trichlorsilane to vinyltrichlorsilane, 1-octane and stirol. Our experiment i.e. the telomerization reaction in the case of methyldichlorsilane, ethyldichlorsilane, triethylsilane with ethylene and propylene in presence of benzoyl-superoxide or tertiary butyle-peroxide at 100-140° and 100-300 atm. overpressure failed. We succeeded only at 260-275° and 560 atm. overpressure. Here we report only on the reaction of trichlorsilane with ethylene. The telomerization reactions which we investigated as well as the affiliation reactions described in publications were at the expense of the Si-H-formation, a fact which is proved by the lack of this binding in the obtained compounds. The construction of the latter is confirmed by the determination of molecule-refraction as well as by the obtaining of corresponding trimethylalkylsilane

Card 1/2

FREEDLINA, R. Kh.

Homolytic isomerization of 1,1-trichloro-2-bromopropene. A. N. Nesmerov, R. Kh. Freidlina, and V. N. Kost (Inst. Heterogeneous Chem., Acad. Sci. U.S.S.R., Moscow). *Doklady Akad. Nauk S.S.S.R.* 113, 824-31 (1957); cf. C.A. 47, 3769c; 51, 1252d. — Keeping a specimen of $\text{CCl}_2\text{CHBr}\cdot\text{CH}_3$ (b_p 57-58°, n_D 1.5333, d₄ 1.5403) 1-2 days or irradiating with ultraviolet light for a few min. results in total isomerization to $\text{CCl}_2\text{CHCH}_2\text{Br}$, b_p 78-80°, 1.5550, 1.8335, which is readily followed by change in n. Hydroquinone or Me₂NPh hinder the isomerization. The reaction is believed to be a radical process with initial cleavage of a Br atom and the attack on an intact mol. at the 2nd C atom. The same starting material undergoes an allylic rearrangement under action of SnCl_4 or AlCl_3 yielding 93% $\text{CCl}_2\text{CHBrCH}_2\text{Cl}$, b_p 81-2°, 1.5523, 1.8354. $\text{CCl}_2\text{CH}\cdot\text{CH}_3$ in AcOH in the dark with Br gave $\text{CCl}_2\text{CHBrCH}_2\text{Br}$ which with KOH in EtOCH₂CH₂OH gave 71% $\text{CCl}_2\text{CHBr}\cdot\text{CH}_3$. $\text{CCl}_2\text{CHCH}_2\text{Cl}$ with Br gave $\text{CCl}_2\text{BrCHBrCH}_2\text{Cl}$ (oxidation with HNO₃ gave $\text{ClCH}_2\text{CHBrCO}_2\text{H}$) which with KOH gave $\text{CCl}_2\text{CHBrCH}_2\text{Cl}$. $\text{CCl}_2\text{CHCH}_2\text{Cl}$ with NaBr in Me₂CO gave $\text{CCl}_2\text{CHCH}_2\text{Br}$. All the trichlorobromopropenes were identified also as solid HCl salts of their Et₃N derivs. prepd. by addn. of Et₃NH in MeOH. $\text{CCl}_2\text{CHBrCH}_2\text{NEt}_3$ b_p 69°, 1.5079, 1.4000; HCl salt, m. 144-5°. $\text{CCl}_2\text{CHCH}_2\text{CH}_2\text{Br}$ and Br in CHCl₃ with illumination gave $\text{CCl}_2\text{CHBrCH}_2\text{Br}$ contaminated by an isomer which was not isolated, but since the mixt. oxidized with HNO₃ gave 20% $\text{BrCH}_2\text{CHClCO}_2\text{H}$, the compd. may be $\text{CCl}_2\text{CHCHClCH}_2\text{Br}$; treatment of the crude mixt. with KOH gave a mixt. of bromotrichloropropenes. The mixt. is explained by a homolytic action of Br in contrast to the reaction in the dark.

G. M. Kozlovskii

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20-114 3-29/60

AUTHORS: Nesmeyanov, A. N., Member of the AS USSR, Freydlina, R. Kh.,
Belichko, F. K.

TITLE: Synthesis and Chemical Transformations of Trichloromethyl and
 ω, ω -Dichlorallyl Compounds of Mercury (Sintez i khimicheskiye
prevrashcheniya trikhlorometil'nykh i ω, ω -dikhloralil'nykh
soyedineniy rtuti)

PERIODICAL: Doklady Akademii Nauk SSSR, 1957, Vol. 114, Nr 3, pp. 557-559 (USSR)

ABSTRACT: As far as organic compounds of mercury containing the tri-
chloromethyl or the dichlorallyl group are interesting from
the point of view of the chemical behavior of these groups,
the authors studied the possibility of a synthesis of such
compounds and several of their transformations. While it
was possible to describe organic mercury compounds contain-
ing the trifluoromethyl or the triiodomethyl group, synthesis
tests of trichloromethyl compounds were frustrated by the de-
carboxylase of mercury trichloracetate or by the photochemical
reaction of tetrachloride with mercury. Hitherto no represen-
tative of the organic mercury compounds containing ω, ω -di-
haloidallyl has been described. The authors investigated the

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20-114-3 29/60

Synthesis and Chemical Transformations of Trichloromethyl and ω, ω -Dichloro-allyl Compounds of Mercury

reactions of bromotrichloromethane, bromo- and iododichloromethane with 1,1-dichloro-3-iodopropene-1 with mercury in the case of ultra-violet irradiation and heating up to $70 - 80^{\circ}\text{C}$ and vigorous stirring; furthermore, the reaction of iodotrichloromethane with mercury in the case of normal agitation without any irradiation was studied. From these processes the following compounds resulted: CCl_3HgBr , CHCl_2HgBr , CHCl_2HgJ , $\text{CCl}_2=\text{CHCH}_2\text{HgJ}$ and CCl_3HgJ with yields 41; 1.2; 2.5; 67 and 12 % according to theory. By the interaction of bromotrichloromethane and a calculated quantity of sodium amalgam of 0.5 % with hexachloro-ethane, one received with a small yield also trichloromethyl-mercury and no symmetric compound $(\text{CCl}_3)_2\text{Hg}$. Such an anomaly is known only in the case of iodocyclohexane-mercury. The authors found a simpler and more convenient method for the transition of alkyl-mercury-iodides to chlorides. It consists of an exchange reaction with mercuric chloride in the case of heating in ether or alcohol. In a number of reactions the 3-methyl compounds of mercury remind one of the so-called "quasi-complex" compounds. Trichloromethyl-

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20-114 3-29/60

Synthesis and Chemical Transformations of Trichloromethyl and ω, ω -Dichloroallyl Compounds of Mercury

-mercury-halogenides form complexes with pyridine as well as "quasi-complex" compounds. In the case of CCl_3HgJ the complex is unstable and disintegrates quickly if stored. Hydrogen sulfide causes HgS already in a cold state to separate quantitatively from the alcohol solution. At interaction of bromotrichloromethyl-mercury with $\text{C}_6\text{H}_5\text{MgBr}$, bromophenyl-mercury is produced beside phenyl-trichloromethyl-mercury. The interaction of bromotrichloromethyl-mercury with diphenylstannian under normal conditions progresses in two different directions according to the quantity of alkali used. With a stoichiometric proportion phenyltrichloromethyl-mercury (49 %) is produced. With a larger quantity of alkali the reaction leads to diphenyl-mercury (29 %). In both cases plenty of infusible and insoluble precipitates containing mercury were produced. With HCl containing methanol phenyltrichloromethyl-mercury forms $\text{C}_6\text{H}_5\text{HgCl}$ with a quantitative yield. The first-mentioned compound, after half an hour of heating in a sealed glass tube, yields the latter with 80 %. The influence of normal "symmetrizers" (KJ , $\text{Na}_2\text{S}_2\text{O}_3$, Cu) upon trichloromethyl-mercury-halogenid-

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Synthesis and Chemical Transformations of Trichloromethyl and ω, ω -Dichloro-allyl Compounds of Mercury

es does not lead to a formation of bistrichloro-methyl-mercury, which does not happen under the influence of dry ammonia upon a chloroform solution of CCl_3HgCl either. In the latter case 95.5 % of an infusible precipitate is produced. There are 1 table and 13 references, 10 of which are Soviet..

ASSOCIATION: Institute for Elemental-Organic Compounds AS USSR
(Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR)

SUBMITTED: December 28, 1956

Card 4/4

AUTHORS

Nesmeyanov, A.N., academician,
Freydlina, R.Kh. and Chukovskaya, E.Ts.

20-4-28/60

TITLE

Thermal Telomerization of Olefins with Silanes
Containing a Si - H Bond.
(Termicheskaya telomerizatsiya olefinov s silanami,
soderzhashchimi Si-H-svyaz')

PERIODICAL

Doklady Akademii Nauk SSSR, 1957, Vol. 115, Nr 4,
pp. 734-736 (USSR)

ABSTRACT

As it was earlier proved by the authors, ethylene enters
a telomerization reaction at 270-300°C under pressure
and when an excess of ethylene is assured. A mixture of
substances $XSiCl_2(CH_2CH_2)_nH$, develops, where $X = Cl, CH_3$.

Propylene under similar conditions also readily enters
the reaction with methyldichlorosilane. It was inter-
esting to find out whether silanes which contain no
haloids also enter this reaction, as well as silanes
whose Si is connected with the aromatic nucleus. The
author found that ethylene readily enters the thermal
telomerization reaction with phenyldichlorosilane. At
280°C and 90 at. superpressure the compounds

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$C_6H_5SiCl_2(CH_2CH_2)_nH$ were obtained, where $n = 1, 2, 3$.

FREYDLINA, R. Kh.

A. N. Nesmeyanov, R. Kh. Freydina, A. A. Karapetyan and Ye. Ts. Chukovskaya,
"The Thermal Telomerization of Silicon Hydrides with Ethylene."

Report presented at the Second All-Union Conference on the Chemistry and
Practical Application of Silicon-Organic Compounds held in Leningrad from
25-27 September 1958.

Zhurnal prikladnoy khimii, 1959, Nr 1, pp 238-240 (USSR)

AUTHORS: Freydlina, R. Kh., Vasil'yeva, Ye. I. 62-1-6/29

TITLE: The Hydrolysis of Polyhaloid Hydrocarbons Containing the CHal_3 - or $\text{CCl}_2=\text{CH}$ -Group (Gidroliz poligaloiduglevodorov, soderzhashchikh CHal_3 ili $\text{CCl}_2=\text{CH}$ -gruppy).

PERIODICAL: Izvestiya AN SSSR Otdeleniye Khimicheskikh Nauk, 1958, Nr 1, pp 35-39 (USSR)

ABSTRACT: It is known that the hydrolysis of the trichloromethyl- and dichlorovinyl-group takes place in consequence of the action of sulphuric acid. If oleum is used the reaction can be carried out (at room temperature). This method can, however, not be used, if α -chlorocarboxylic acids are obtained by means of the hydrolysis of the compounds which contain the $\text{CCl}_3\text{-CHCl}$ -group. In the present paper the hydrolysis of the series of the α, α, α -trichloro- and $\alpha, \alpha, \alpha, \omega$ -tetrachloroalkanes with nitric acid (specific weight 1,51-1,52) was realized. Furthermore it was shown that the highest trichloro- and tetrachloroalkanes (with the atomic number of the carbon in the molecule 11, 13, 15, 17) are evenly hydrolysed by nitric acid. Here the corresponding carboxylic and ω -chlorocarboxylic acids with the same number of atoms of carbon in the molecule are formed. The hydrolysis of the

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The Hydrolysis of Polyhaloid Hydrocarbons Containing the
CHal₃- or CCl₂ CH-Group.

62-1-6/29

fatty compounds containing a CHBr-CCl₂Br-grouping takes place under the influence of the nitric acid (specific weight 1,52) with a high yield of the corresponding α-bromocarboxylic acids. The concentrated sulphuric- or 70%-perchloric acid do not hydrolyse the compounds of the above mentioned structure. Perchloric acid of 70% hydrolyses fatty - as well as aromatic compounds (containing the CCl₂- or CCl₂CH-group) to corresponding carboxylic acids. The reaction takes place under comparatively hard conditions (at 115-130°). There are 15 references, 5 of which are Slavic.

ASSOCIATION: Institute of Elemental-Organic Compounds, AS USSR (Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR).

SUBMITTED: July 14, 1956

AVAILABLE: Library of Congress

1. Polyhaloid hydrocarbons-Hydrolysis

Card 2/2

FREYDLINA, R. KH.
 AUTHORS: Nesmeyanov, A. N., Freydlina, R. Kh., Velichko, F.K. 62-1-7/29

TITLE: Synthesis and Properties of the Trichloromethyl and α, α' -
 -Dichloroallyl Compounds of Mercury (Sintez i svoystva
 trikhlorometil'nykh i α, α' -dikhloralil'nykh soyedineniy rtuti)

PERIODICAL: Izvestiya AN SSSR Otdeleniye Khimicheskikh Nauk, 1958, Nr 1,
 pp 40-45 (USSR)

ABSTRACT: After the authors have been occupied for the last years with
 the research of the chemical transformations of the trichloro-
 methyl- and asymmetric dichlorovinyl group in polychloro-
 hydrocarbons (and similar compounds), it was of interest to
 investigate the properties of organomercuric compounds which
 contain the above mentioned compounds. Interesting is also
 the investigation of the properties of the radicals $\text{CCl}_3 \cdot$
 and $\text{CCl}_2=\text{CHCH}_2 \cdot$, formed by the decomposition of the
 organomercuric compounds. One succeeded hitherto neither ab-
 road nor in the USSR in carrying out the synthesis of the
 trichloromethyl compounds. The experiments of Karash and
 Stavli remained without success. Not even one representative
 of the α, α' -dihaloidallyl organomercuric compounds has
 hitherto been described in literature. Bromotrichloromercury
 was synthesized by the reaction of mercury with brometri-

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Synthesis and Properties of the Trichloromethyl and γ, γ -
-Dichloroallyl Compounds of Mercury

62-1-7/29

chloromethane; from the latter hydroxide, chloride, and iodide of the trichloromethylmercury were obtained the normal way. Phenyltrichloromethylmercury was synthesized by the interaction between bromotrichloromethylmercury and dichlorodiphenyl-tin in an alkaline medium. The reaction of same with hydrochloric acid led to the formation of chlorophenylmercury. The halides of trichloromethylmercury form complex compounds with pyridine. The double compound of pyridine with bromotrichloromethylmercury outlasts the recrystallization and shows a composition of $\text{CCl}_3\text{HgBr} \cdot \text{C}_5\text{H}_5\text{N}$. Ammonia and hydrogen sulfide destroy completely the halides of trichloromethylmercury. 3-iodide mercury-1 and 1-dichloropropene-1 were synthesized by reaction of 3-iodide-1, 1-dichloropropene-1, and mercury under action of ultraviolet light; from it 3-chloromercury- and 3-bromomercury-1, 1-dichloropropene-1 was obtained the usual way. There are 13 references, 6 of which are Slavic.

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ASSOCIATION: Institute of Elemental-Organic Compounds, AS USSR (Institut
elementoorganicheskikh soedineniy Akademii nauk SSSR)
SUBMITTED: July 14, 1956

1. Mercury compounds (Organic)-Synthesis 2. Mercury compounds
(Organic)-Properties

Freydlina R. Kh.

62-2-4/28

AUTHORS: Nesmeyanov, A. N., Kost, V. N.,
Vasil'yeva, T. T., Freydlina, R. Kh.

TITLE: The Synthesis of α -Haloidcarboxylic Acids Containing Reactive Groups in the ω -Position (Sintez α -galoidkarbonovykh kislot, soderzhashchikh v ω -polozhenii reaktivnykh gruppy).

PERIODICAL: Izvestiya AN SSSR Otdel'nye Khimicheskikh Nauk, 1958, Nr 2, pp. 152-156 (USSR).

ABSTRACT: As was already shown (references 1,2) α -perchloric acids can easily be produced in a sulfate medium by the action of chlorine upon compounds containing a $\text{CCl}_2 = \text{CH}$ -group. A similar reaction also takes place in perchloric acid. In the series of cases hitherto investigated the experiment failed in the medium of phosphoric acid and acetic acid (reference 2). The employment of this method in compounds possessing no stable groups in a medium of strong acids is therefore not possible. In the present work it was found that the compounds of the type $\text{CCl}_2 = \text{CX}(\text{CH}_2)_n \text{Y}$ (where X is a halide or H, and where Y represents various groups) interact with acetic acid and the halide in the presence of mercury acetate after treatment with H_2O . On this occasion α -haloidcarboxylic acids or .

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The Synthesis of α -Haloidcarboxylic Acids Containing Reactive Groups in the ω -Position. 62-2-4/28

α, α -dihaloidcarboxylic acids form.

In this manner the following acids were produced:

$\text{Cl}(\text{CH}_2)_3\text{CHClCOOH}$; $\text{Cl}(\text{CH}_2)_3\text{CHBrCOOH}$; $\text{CH}_3\text{COO}(\text{CH}_2)_3\text{CHClCOOH}$;

$\text{CN}(\text{CH}_2)_3\text{CHClCOOH}$; $\text{CH}_3\text{COOCH}_2\text{CHClCOOCH}_3$; $\text{CH}_3\text{OCH}_2\text{CHClCOOH}$;

$\text{C}_6\text{H}_5\text{CH}_2\text{CHClCOOH}$; $\text{Cl}(\text{CH}_2)_3\text{CCl}_2\text{COOH}$.

There are 6 references, 5 of which are Slavic.

ASSOCIATION: Institute for Element-Organic Compounds AN USSR (Institut elementoorganicheskikh soedineniy Akademii nauk SSSR).

SUBMITTED: September 25, 1956

AVAILABLE: Library of Congress

1. Perchloric acids 2. α -Haloidcarboxylic acids-Synthesis

Card 2/2

62-58-3-5/30

AUTHORS: Petrova, R. G. , Freydina, R. Kh.

TITLE: The Synthesis of Mercaptanes, Sulfides and Sulfo Acids Containing Trichloromethyl-, Dichlorovinyl- or Carboxyl Groups (Sintez merkaptanov, disul'fidov i sul'fokislot, soderzhashchikh trikhlorometil'nyye, dikhlorvinil'nyye ili karboksil'nyye gruppy)

PERIODICAL: Izvestiya Akademii Nauk SSSR Otdeleniye Khimicheskikh Nauk, 1958, Nr 3, pp. 290 - 295 (USSR)

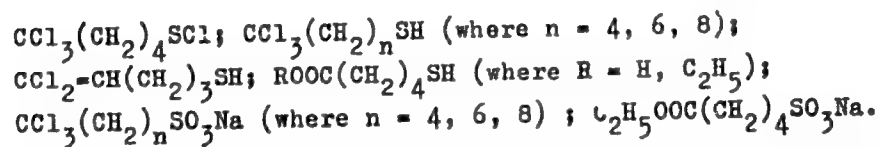
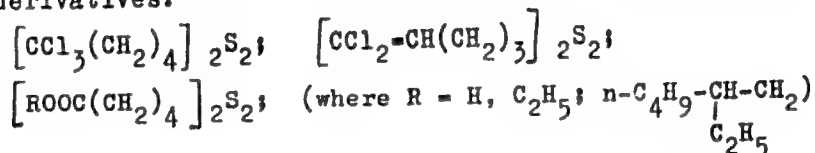
ABSTRACT: The synthesis of titanium sulfides described in the preceding paper by Nesmeyanov, Zakharkin and Petrova started from $\alpha, \alpha, \alpha, \omega$ -tetrachloroalkanes. It was of interest also to synthesize compounds with other functions, chiefly sulfurous ones, from the $\alpha, \alpha, \alpha, \omega$ -tetrachloroalkanes. No data were published on a synthesis of compounds of the type $\text{SH}(\text{CH}_2)\text{CH}=\text{CCl}_2$ as well as others (References I, III, IV, V, VI, VII, and VIII). Starting from the above-mentioned tetrachloroalkanes and trichloroalkanes with the structure $\text{CCl}_2-\text{CH}(\text{CH}_2)_n\text{Cl}$ and ω -chlorocarboxylic acids the authors synthesized:

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62-58-3-5/30

The Synthesis of Mercaptanes, Sulfides and Sulfo Acids Containing Trichloromethyl-, Dichlorovinyl- or Carboxyl Groups

dithio-mercaptano- and sulfo compounds as well as some derivatives:



There are 1 table and 6 references, 2 of which are Soviet.

ASSOCI ION: Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR (Institute for ~~Elemental~~ Organic Compounds, AS USSR)

SUBMITTED: November 17, 1956

Card 2/2

FREYDLINA, R.Kh.

AUTHOR:

None given

02-58-4-30/32

TITLE:

Anniversary Session of the Department
for Chemical Sciences of the AS USSR on October 30 and 31,
1957, and General Meeting of the Department for Chemical
Sciences on December 19 and 20, 1957 (Yubileynaya sessiya
otdeleniya khimicheskikh nauk Akademii nauk SSSR ot 30-31
oktyabrya 1957 g. i obshcheye sobraniye otdeleniya khimicheskikh nauk 19-20 dekabrya 1957 g.)

PERIODICAL:

Izvestiya Akademii Nauk SSSR, Otdeleniye Khimicheskikh Nauk,
1958, Nr 4, pp. 521 - 524 (USSR)

ABSTRACT:

On the occasion of the 40th anniversary of the October
Revolution a reunion meeting of the Department for Chemical
Sciences of the AS USSR took place. In his opening speech
N. N. Semenov pointed out the outstanding success of the USSR
in the field of sciences especially in that of chemistry.
Scientific lectures of the sessions were held by the following
scientists, as was mentioned already earlier: Knunyants,
Member, Academy of Sciences, and A. V. Fokin on the "Nitration
of Fluorofines", A. L. Midzhoyan, Member, AS Armenian SSR,

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62-58-4-30/32

Anniversary Session of the Department for Chemical Sciences of the AS USSR on October 30 and 31, 1957, and General Meeting of the Department for Chemical Sciences on December 19 and 20, 1957.

on the "Investigations in the Field of the Synthesis of Physiologically Active Compounds", R. Kh. Freydlina, Doctor of Chemical Sciences, reported on the "Investigation of the Telomerization Reaction and the Reaction of the Synthesis on the Basis of Telomers" (Reference 2). B. A. Dolgoplosk, Doctor of Chemical Sciences, spoke on the "Generation of Free Radicals in Solutions and Their Reactions in Model Systems," A. M. Frumkin, Member of the Academy of Sciences, reported on "Some General Problems of Electrochemical Kinetics and the Theory of Ion Reactions" (Reference 4), A. V. Kiselev, Doctor of Chemical Sciences (Reference 5) spoke on "Some Problems of Adsorption Theory", H. H. Emanuel (Reference 6), Doctor of Chemical Sciences, reported on "New Problems in the Field of Chain Reactions", V. L. Tal'roze, Candidate of Chemical Sciences, spoke on mass-spectroscopic investigations of ion-and radical reactions, A. P. Rebinder, Member,

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62-58-4-30/32

Anniversary Session of the Department for Chemical Sciences of the AS USSR on October 30 and 31, 1957, and General Meeting of the Department for Chemical Sciences On December 19 and 20, 1957

Academy of Sciences, drew conclusions with regard to the development of physico-chemical mechanics (Reference 7). I. V. Tananayev, Corresponding Member of the AS USSR, gave new data on the chemistry of some rare elements, D. I. Ryabchikov and others spoke on the "Problems of the Chemistry of Rare Earth Elements"; the final lecture was that of V. A. Sokolov, Doctor of Chemical Sciences, on the "Calorimetric Measurements at High Temperatures". General Regular Meeting of the Department for Chemistry of the AS USSR (December 19 - 20, 1957): A. I. Brodskiy, Corresponding Member, AS USSR, spoke on the "Investigation of Some Reactions of Peroxides and Peracids of Hydrogen by Means of the Isotopic Method", M. K. Shemyakin, Corresponding Member, AS USSR, spoke on the "Use of N¹⁵ for the Explanation of the Mechanism of Some Organic Reactions", O. A. Reutov, Doctor of Chemical Sciences, reported on the "Investigation of the

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62-56-4-30/32

Anniversary Session of the Department for Chemical Sciences of the AS USSR on October 30 and 31, 1957, and General Meeting of the Department for Chemical Sciences On December 19 and 20, 1957

Electrophil and Homolytical Reactions of the Substitution in the Carbon Atom by Means of the Method of Isotope Exchange", I. P. Alimarin, Corresponding Member, AS USSR, reported on new methods of determination of the division of rare elements using organic derivative sulfuric-, selenic- and telluric acids, V. G. Levich, Doctor of Chemical Sciences, reported on the "Diffusion Kinetics of Heterogenous Chemical Reactions in mobile Liquids". There are 8 references, all of which are Soviet.

AVAILABLE: Library of Congress

1. Chemical industry--USSR

Card 4/4

AUTHORS: Mesmeyanov, A. N., Vasil'yeva, Ye. I., SOY/62-58-7-6/26
 Freydlina, R. Kh.

TITLE: ω, ω' -Imino Dicarboxylic Acids and Some of Their Derivatives
 (ω, ω' -Iminodikarbonovyye kisloty i nekotoryye ikh proizvodnyye)

PERIODICAL: Izvestiya Akademii nauk SSSR, Otdeleniye khimicheskikh nauk,
 1958, Nr 7, pp 836 - 840 (USSR)

ABSTRACT: In the present paper the authors describe the synthesis of the
 dicarboxylic acids of the type A $[(CH_2)_n COOH]_2$, where A re-
 presents NH, and n is equal to 6, 8, 10 (as well as their N- and
 O-derivatives). In publications the imino dicarboxylic acids,
 the ω, ω' -iminodipropionic and ω, ω' -iminodieneanthylic acids
 (Ref 5) of these compounds have been described. Proceeding from
 the ω -chlorocarboxylic acids the authors produced ω, ω' -imino
 dicarboxylic acids as well as their N- and O-derivatives. They
 investigated in detail the chemical reactions of ω, ω' -imino di-
 eneanthylic acid. The following derivatives were obtained from
 this acid: diethyl ester, the N-acetyl derivative, the N-methyl
 derivative of the acids and their esters, the monoethyl ester of
 the monoamide, the chlorohydrate of the diamide and the chloro-

Card 1/2

α, ω' -Imino Dicarboxylic Acids and Some of Their
Derivatives

SOV/62-58-7-6/26

hydrate of the monoethyl ester of N-methyl-imino dieneanthylic
acid. There are 7 references, 5 of which are Soviet.

ASSOCIATION: Institut elementoorganicheskikh soedineniy Akademii nauk SSSR
(Institute of Elemental-organic Compounds, AS USSR)

SUBMITTED: December 25, 1956

Card 2/2

AUTHORS: Nesmeyanov, A. N., Zakharin, L. I., SOV/62-58-7-7/26
 Freydlina, R. Kh.

TITLE: Amines Containing the CCl_3 Group and Their Basicity (Aminy, soderzhashchiye CCl_3 gruppu i ikh osnovnost')

PERIODICAL: Izvestiya Akademii nauk SSSR, Otdeleniye khimicheskikh nauk, 1958, Nr 7, pp 841 - 845 (USSR)

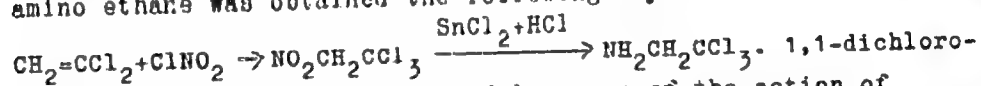
ABSTRACT: The aim of the present paper was the explanation of the influence of the CCl_3 group on the basicity of the amino group in the $\text{NH}_2(\text{CH}_2)_n\text{CCl}_3$ series. The values of the dissociation constants K , obtained are shown in table 1. The dissociation constants K for ethyl amine, propyl amine and n.butyl amine amount to $3.4 \cdot 10^{-4}$ (25°), $4.7 \cdot 10^{-4}$ (25°), $4.1 \cdot 10^{-4}$ (25°). It may be seen that by the introduction of the trichloro-methyl group instead of the methyl group the amino basicity is decreased by the 10^4 fold if the CCl_3 and NH_2 group is divided by a methylene group. If the CCl_3 group is compared to the CCl_2CH group it may be seen that the former has a considerably greater induction effect (of the electron acceptor) than the latter. The amine

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Amines Containing the CCl_3 Group and Their Basicity

SOV/62-58-7-7/26

synthesis was achieved the following way: 1,1,1-trichloro-3-aminopropane, 1,1,1-trichloro-4-aminobutane, and 1,1-dichloro-4-aminobutene-1 were obtained from the corresponding carboxylic acids under the action of nitrous hydrogen acid in the presence of concentrated sulfuric acid. The amine yield is, however, small due to the side reactions of the dehydrochlorination and the hydrolysis under the action of sulfuric acid. 1,1,1-trichloro-2-amino ethane was obtained the following way:



1,1-dichloro-3-aminopropene-1 was synthesized by means of the action of hexamethylene tetraamine on 1,1,3-trichloro-propene-1 with a subsequent adduct decomposition by hydrochloric acid.

Conclusion: The dissociation constants of the amines of the $\text{CCl}_3(\text{CH}_2)_n\text{NH}_2$ series were measured, with n being equal to 1-4, and the $\text{CCl}_2=\text{CH}(\text{CH}_2)_n\text{NH}_2$ series, with n being equal to 1,2.

There are 2 tables and 5 references, 4 of which are Soviet.

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Amines Containing the CCl_3 Group and Their Basicity

SOV/62-58-7-7/26

ASSOCIATION: Institut elementoorganicheskikh soedineniy Akademii nauk SSSR
(Institute of Elemental-organic Compounds, AS USSR)

SUBMITTED: December 28, 1956

Card 3/3

SOV/62-58-8-4/22

AUTHORS:

Braynina, E. M., Freydlina, R. Kh., Mesmeyanov, A. N.

TITLE:

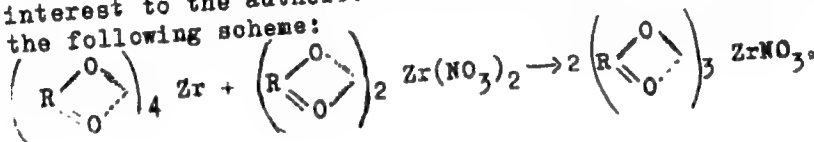
The Reaction of the Reverse Disproportioning Within the Series of Chelate Zirconium Compounds (Reaktsiya, obratnaya disportsionirovaniyu, v ryadu kleshneobraznykh soyedineniy tsirkoniya)

PERIODICAL:

Izvestiya Akademii nauk SSSR, Otdeleniye khimicheskikh nauk, 1958, Nr 8, pp. 937-940 (USSR)

ABSTRACT:

In the previous paper some exchange reactions of chelate zirconium compounds were described. In the present paper the authors describe other reactions of the same type. The reaction of the reverse disproportioning realized by the example of the interaction of zirconium tetraacetyl acetate with the dintrate of zirconium diacetyl acetate was of the greatest interest to the authors. The reaction took place according to the following scheme:



Card 1/2

FREYDLINA, R.Kh.

pr
AUTHOR: None Given SOV/62-58-8-22/22

TITLE: The General Meeting of the Department of Chemical Sciences of the AS USSR From April 24 to 25, 1958 (Obshcheye sobraniye otdeleniya khimicheskikh nauk AN SSSR ot 24-25 aprelya 1958 g.)

PERIODICAL: Izvestiya Akademii nauk SSSR, Otdeleniye khimicheskikh nauk, 1958, Nr 8, pp. 1017 - 1018 (USSR)

ABSTRACT: At this General Meeting the following scientists delivered lectures: The Corresponding Members, Academy of Sciences, USSR, A. A. Grinberg, I. A. Kazarnevskiy, A. D. Petrov, and R. Kh. Freydlina, Doctor of Chemical Sciences. A. A. Grinberg reported on the new knowledge on the kinetics and the mechanism of the reactions of the exchange and the substitution in complex compounds of platinum. Based on experimental data the lecturer concluded that in the process of the isotopic exchange in the derivatives of bivalent palladium the dissociation and association mechanism play an important role. These explanations raised a vivid discussion in which mainly I. I. Chernyzyev, Member, Academy of Sciences, USSR and the Corresponding Members, Academy of Sciences, USSR V. I. Spitsin, Ya. K. Syrkina, I. V. Tananayev, and A. D. Gelman, Doctor of Chemical Sciences, took part. I. A.

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SOV/62-58-8-22/22

The General Meeting of the Department of Chemical Sciences of the AS USSR
From April 24 to 25, 1959

Kazarnovskiy held a lecture on the investigations of the kinetics and the mechanism of the arbitrary decomposition of potassium ozonide (employing the magnetic method) carried out by himself and his collaborators (S. I. Reykhshteyn and L. N. Bykova, Candidates of Chemical Sciences). A. D. Petrov on behalf of the collaborators of the Institute of Organic Chemistry (V. F. Mironov, V. A. Ponomarenko, S. I. Sadykh-Zade and Ye. A. Chernyshev) reported on "The Synthesis of New Forms of Silicon Containing Monomers". He announced new results of investigations of the catalytic binding of hydride silanes with unsaturated and aromatic compounds not published up to now. In the discussion following this lecture V. V. Korshak, Corresponding Member, Academy of Sciences, USSR, said that the results obtained by the team of A. D. Petrov were of great importance. The corresponding conclusions had to be drawn from the influence exerted by silicon in the various groups on the reactivity of these compounds. The report delivered by R. Kh. Freydlina on "The Homolytic Isomerization in Solutions" raised great interest. This lecture was followed by a vivid exchange

Card 2/3

AUTHORS: Nesmeyanov, A. N., Freydlina, R. Zh., SOV/62-58-10-6/25
Kost, V.N.

TITLE: Homolytic Isomerization of 1,1,1-Trichloro-2-Bromo Propene
(Gomoliticheskaya izomerizatsiya 1,1,1-trikhlor-2-brompropena)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,
1958, Nr 10, pp 1199-1204 (USSR)

ABSTRACT: The possibility of regrouping the free radicals in solutions
has been proved in several papers (Refs 4-9). In a number of
other papers (Refs 9, 11, 12) it was shown that the neopentyl
radical can be isomerized. Therefore in publications data are
given that contradict each other with respect to the possibility
of a regrouping of the radicals (at the expense of the migration
of methyl groups). In the present paper the authors report on
the homolytic isomerization of 1,1,1-trichloro-2-bromo propene
in 1,1,2-trichloro-3-bromo propene-1 according to the scheme

$$\text{CCl}_3\text{CBr} = \text{CH}_2 \longrightarrow \text{CCl}_2 = \text{CCl} - \text{CH}_2\text{Br}.$$

Furthermore the authors deal with a case of homolytic
isomerization of $\text{CCl}_3\text{CBr} = \text{CH}_2$ discovered by themselves. They

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Homolytic Isomerization of 1,1,1-Trichloro-2-Bromo
Propene

SOV/62-58-10-6/25

show that 1,1,1-trichloro-2-bromo propene executes the allyl regrouping (under the action of antimony pentachloride or aluminum chloride). Then 1,1,3-trichloro-2-bromo propene-1 is formed. Under the action of caustic potash on 1,1,1-trichloro-2,3-dibromo propene in ethyl-cellosolve medium the 1,1,1-trichloro-2-bromo propene was obtained as the only product of the reaction. Its isomerization takes place in a homolytic way under the action of ultraviolet rays and with a simultaneous formation of 1,1,2-trichloro-3-bromo propene; 1,1,1-trichloro propene isomerizes according to the heterolytic way under the action of antimony pentachloride with the simultaneous formation of 1,1,3-trichloro-2-bromo propene. There are 22 references, 5 of which are Soviet.

ASSOCIATION: Institut elementoorganicheskikh soeylineniy Akademii nauk SSSR
(Institute of Elementary Organic Compounds, Academy of
Sciences, USSR)

SUBMITTED: March 7, 1957
Card 2/2

AUTHORS: Nesmeyanov, A. N., Freydlina, R. Kh., SOV/62-58-10-7/25
Kost, V. N.

TITLE: Bromination of 1,1,1-Trichloropropene
(Bromirovaniye 1,1,1-trikhlorpropena)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,
1958, Nr 10, pp 1205-1207 (USSR)

ABSTRACT: Two of the authors mentioned above together with Firstov described in an earlier paper the bromination of 1,1,1-trichloropropene (Ref 1). In a later paper they found the regrouping of the intermediately forming free radical (Ref 2) when investigating the reaction of hydrogen bromide and bromo-trichloromethane with 1,1,1-trichloropropene in the presence of benzoyl peroxide. It was assumed that (dependent on the conditions of reactions) the bromination of 1,1,1-trichloropropene takes place without regrouping (electrophilic reaction) or with it (homolytic reaction). The authors of the present paper investigated the reaction of the bromination of 1,1,1-trichloropropene and obtained the following results: In highly polar media the reaction takes place well defined with the simultaneous formation of the normal

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SOV/62-58-10-7/25

Bromination of 1,1,1-Trichloropropene

combination product of 1,1,1-trichloro-2,3-dibromopropane. If the reaction is carried out in unpolar media 1,1,2-trichloro-1,3-dibromo propane (due to the homolytic isomerization of the not intermediately formed free radical $\text{CCl}_3\dot{\text{C}}\text{H} - \text{CH}_2\text{Br} \rightarrow \dot{\text{C}}\text{Cl}_2\text{CHCl} - \text{CH}_2\text{Br}$) is formed. There are 6 references, 5 of which are Soviet.

ASSOCIATION: Institut elementoorganicheskikh soedineniy Akademii nauk SSSR
(Institute of Elementary Organic Compounds, Academy of Sciences USSR)

SUBMITTED: March 7, 1957

Card 2/2

5(3)

AUTHORS:

Nesmeyanov, A. N., Academician, SOV/20-122-5-20/56
~~Freydlina, R. Kh.~~, Corresponding Member, Academy of
Sciences, USSR, Belyavskiy, A. B.

TITLE:

Telomerization of Ethylene With Tetrachlorethylene
(Telomerizatsiya etilena s tetrakhloretilenom)

PERIODICAL:

Doklady Akademii nauk SSSR, 1958, Vol 122, Nr 5,
pp 821 - 824 (USSR)

ABSTRACT:

Non-polymerizable chlorine olefins cannot undergo any polymerization, but they can enter a telomerization reaction with olefins. In this reaction the chlorine olefins serve as carriers of the chain of reaction and supply the final groups for the telomer molecules. Among the reactions of this kind the ones mentioned in the title are of interest as means of synthesis of tetrachloralkenes capable of reaction that contain an even number of carbon atoms in the molecule (Scheme (1)). It can be assumed that tetrachloralkenes produced in this manner will make possible the synthesis of various polyfunctional compounds of the even series

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Telomerization of Ethylene With Tetrachlorethylene

SOV/20-122-5-20/56

(Ref 1). The reaction mentioned in the title must lead to the synthesis in one single stage of compounds containing a trichlorovinyl group (Patent in reference 2). In the reaction performed in the presence of benzoyl peroxide at 115° and 95 atmospheres only tetrachlorohexene boiling in a wide range was isolated. For this the authors used a pressure of between 50 and 200 atmospheres with and without water. Benzoyl peroxide, tertiary butyl peroxide, bis-iso-butyric acid azo-dinitrile and azo-amino-benzene were tested as initiators. In the presence of water a high conversion of tetrachlorethylene was obtained in all cases. Peroxides were the best initiators among the ones tested. Research showed that tetrachlorethylene is a carrier of the chain of reaction which is less capable of reaction as, for instance, carbon tetrachloride and chloroform. Thus, with the first substance a conversion of only 20% was obtained and only in case of repeated addition of the initiator during reaction. In case of an increase of pressure the content of higher tetrachloralkenes in the mixture

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Telomerization of Ethylene With Tetrachlorethylene

SOV/20-122-5-20/56

of reaction products increases which indicates an inertness of tetrachlorethylene. By fractioning the mixture the lower $\alpha, \alpha, \beta, \omega$ -tetrachloralkenes ($n=1.2$) could easily be isolated in their individual shapes. Higher fractions contain by-products of the reaction which could not easily be separated. Still it was possible to obtain tetrachloralkenes with 4,6 and 8 carbon atoms in the molecule and to study some of these chemical transformations. There are 3 references, 2 of which are Soviet.

SUBMITTED: July 5, 1958

Card 3/3

5(3)

PHASE I BOOK EXPLOITATION

SOV/1765

Freydlina, Rakhil' Khatskelevna, and Shavarsh Avetisovich Karapetyan,

Telomerizatsiya i novyye sinteticheskiye materialy (Telomerization and New Synthetic Materials) Moscow, Izd-vo AN SSSR, 1959. 103 p. 20,000 copies printed.

Sponsoring Agency: Akademiya nauk SSSR. Redkollegiya nauchno-populyarnaya seriya.

Ed. of Publishing House: O.M. Yenisherilova; Tech. Ed.: I.N. Guseva.

PURPOSE: This booklet is meant for the general reader who has a secondary school knowledge of the principles of chemistry and physics.

COVERAGE: The authors describe what is said to be a new method for the preparation of synthetic materials which is based on the reaction of telomerization. Cheap raw materials such as natural and industrial gases may be used in the production of new synthetic fibers, plastics, aromatic principles, and other industrial products. A detailed description is given of the manufacture and properties of "enant", a synthetic fiber which is said to have better properties than capron or nylon. The book is based on the results of research by several groups of scientists. R. Kh. Freydlina, Corresponding Member of the AS SSSR, wrote the section on telomerization and the chapter on Conversion of telomers. The other parts were written by Sh. A. Karapetyan. The author thanks G.L. Slonimskiy and T.I. Sheyn for their help in preparing the book. There are 7 references: all Soviet.

5(3)
AUTHORS:

SOV/62-59-4-13/42
Freydlina, R. Kh., Semenov, N. A., Nesmeyanov, A. N.

TITLE:

Synthesis of Aromatic Compounds of the Types $\text{ArCH}_2\text{CH-CCl}_2$ and $\text{Ar' (CH}_2\text{CH-CCl}_2)_2$ (Sintez aromaticheskikh soyedineniy tipa $\text{ArCH}_2\text{CH-CCl}_2$ i $\text{Ar' (CH}_2\text{CH-CCl}_2)_2$)

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 4, pp 652-656 (USSR)

ABSTRACT:

It has already been shown (Refs 1 and 2) that 1,1,1-trichloropropene and 1,1,3-trichloropropene-1 condense with benzene and some other aromatics in the presence of aluminum chloride to form compounds having the structure $\text{ArCH}_2\text{CH-CCl}_2$. In the present work the synthesis of substances of this type was continued and some of their conversions were investigated. In addition, aromatic compounds containing γ,γ -dichloroallyl groups were synthesized. As the condensation in the presence of aluminum chloride is very violent and accompanied by saponification it was attempted to effect the reaction in the presence of other Friedel-Crafts catalysts (SnCl_4 , ZnCl_2 , SbCl_5). The reaction

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SOV/62-59-4-13/42

Synthesis of Aromatic Compounds of the Types $\text{ArCH}_2\text{CH}=\text{CCl}_2$ and $\text{Ar}'(\text{CH}_2\text{CH}=\text{CCl}_2)_2$

was found to proceed smoothly in the presence of antimony pentachloride. The process can be controlled and the reaction mixture is homogeneous. The condensation of 1,1,3-trichloropropene-1 with toluene in the presence of SbCl_5 gave 3-(p-toluenyl)-1,1-dichloropropene-1 in a yield of 80%. The introduction of two γ,γ -dichloroallyl groups into the aromatic nucleus takes place in one or two stages. The interaction of equimolar quantities of naphthalene and 1,1,3-trichloropropene-1 in heptane in the presence of aluminum chloride or tin chloride gives mixtures of mono- or dialkylated products. The condensation of 3-(p-chlorophenyl)-1,1-dichloropropene-1 with 1,1,3-trichloropropene-1 in the presence of aluminum chloride gave a compound of the composition $\text{ClC}_6\text{H}_3(\text{CH}_2\text{CH}=\text{CCl}_2)_2$. The interaction of 3-phenyl-1,1,1,2-tetrachloropropane with 1,1,3-trichloropropane in the presence of SbCl_5 gave a compound $\text{p-CCl}_2=\text{CHCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{CHClCCl}_3$. Its structure was proved by oxidation. The interaction of benzene with 1,1,1,3-tetrachloropropane in the presence of SbCl_5 gave 3-phenyl-1,1-dichloro-

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SOV/62-59-4-13/42
Synthesis of Aromatic Compounds of the Types $\text{ArCH}_2\text{CH}=\text{CCl}_2$ and $\text{Ar}'(\text{CH}_2\text{CH}=\text{CCl}_2)_2$

propene-1 and 3-(p-phenylene)-bis-1,1-dichloropropene-1. The oxidation of 3-(p-chlorophenyl)-1,1-dichloropropene-1 with aqueous nitrogenous acid gave p-chlorocinnamic acid. There are 7 references, 6 of which are Soviet.

ASSOCIATION: Institut elementoorganicheskikh sovedineniy Akademii nauk SSSR
(Institute of Elemental-organic Compounds of the Academy of Sciences, USSR)

SUBMITTED: July 13, 1957 (initially) and April 14, 1958 (after revision)

Card 3/3

5(3)
AUTHORS: Nesmeyanov, A. N., Freydlina, R. Kh., Petrova, R. G.,
Terent'yev, A. B. SOV/62-59-A-14/42

TITLE: Interaction of 1,1,1-Trichloropropene With Sulphene Chlorides
and Sulphur Dichloride (Vzaimodeystviye 1,1,1-trikhlorpropena s
sul'fenkhloridami i dvukhloristoy seroy)

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,
1959, Nr 4, pp 657-662 (USSR)

ABSTRACT: In the present work the addition of phenyl-, benzil-, 2,4-di-
nitrophenyl-, 2-nitrophenyl sulphene chloride and sulphur di-
chloride to 1,1,1-trichloropropene was investigated. The addi-
tion of phenyl sulphene chloride to 1,1,1-trichloropropene gave
1,1,1,3-tetrachloroisopropylphenylsulphide as the main product.
The dehydrochlorination of 1,1,1,3-tetrachloroiso propyl phenyl
sulphide with alkali in ethyl Cellosolve gives a mixture the
composition of which depends mainly on the reaction conditions.
The investigation of the reactions of other sulphene chlorides
shows that 2,4-dinitro- and 2-nitrophenyl sulphene chlorides do
not associate with 1,1,1-trichloropropene under the assumed
conditions. The reaction of 1,1,1-trichloropropene with benzil

Card 1/2

SOV/62-59-4-14/42

Interaction of 1,1,1-Trichloropropene With Sulphene Chlorides and Sulphur Dichloride

sulphene chloride is more complicated and forms mainly a dehydrochlorinated adduct. The consideration of the reaction of 1,1,1-trichloropropene with sulphur dichloride, 2,4-dinitro- and 2-nitrophenyl sulphene chloride shows a similarity between the action of the $-CCl_3$ group having no double bond on the next double bond and the action of other acceptor groups having π -bonds. Sulphur dichloride reacts with 1,1,1-trichloropropene to form 1,1,1,3-tetrachloroisopropyl sulphene chloride. There are 6 references, 4 of which are Soviet.

ASSOCIATION: Institut elementoorganicheskikh soedineniy Akademii nauk SSSR
(Institute of Elemental-organic Compounds of the Academy of Sciences, USSR)

SUBMITTED: July 13, 1957

Card 2/2

5 (3)

AUTHORS:

Freydlina, R. Kh., Kost, V. N.,
Vasil'yeva, T. T., Nesmeyanov, A. N.

SOV/62-59-5-10/40

TITLE:

Synthesis of D,L- α -aminocarboxylic Acids From Compounds Con-
taining the $\text{CCl}_2=\text{CH}$ Group (Sintez D,L- α -aminokarboksyl'nykh kisl'ot
iz soyedineniy soderzhashchikh $\text{CCl}_2=\text{CH}$ -gruppuy)

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,
1959, Nr 5, pp 826 - 830 (USSR)

ABSTRACT:

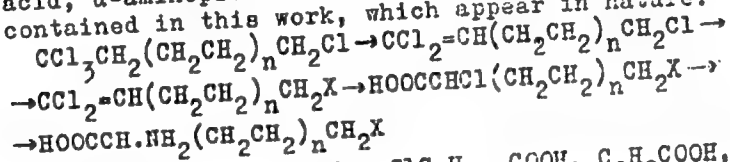
In this work the ammonolysis of some α -chlorocarboxylic acids was investigated which had been synthesized from tetrachloroalkanes by the effect of sulfuric acid or acetic acid in the presence of mercury acetate. This investigation was carried out in order to find a way of synthesizing amino acids and their analogues appearing in nature from tetrachloroalkanes. The synthesis is rather difficult and, in the case of chlorine derivatives, the yield is small according to data from publications. Two authors of this work and Petrov (Ref 7) succeeded in synthesizing D,L-proline and D,L-ornithine from α,δ -dichloro- and α -chloro- δ -phthalimidovalerianic acid; they showed that the yield does not depend on the nature of the halogen in α -position. In this work the initial products α -chlorodipinic, α -

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SOV/62-59-5-10/40

Synthesis of D,L- α -aminocarboxylic Acids From
Compounds Containing the $\text{CCl}_2=\text{CH}$ Group

chloropimelic, and α -chlorosuberic acid were obtained (Ref 2); α -chloroglutaric acid and α -chloro- β -(p-chlorophenyl)propionic acid (Ref 8) and α -chloro- ϵ -phthalimidoheptanoic acid were obtained under the same conditions from 1,1-dichloro-6-phthalimidoheptene-1 and 1,1-dichloro-3-(p-chlorophenyl)propene. The best method was that of the synthesis of α -chloro- β -phenylpropionic acid from chlorophenyldiazonium and acrylonitrile according to the Merrwein reaction (Ref 10) with subsequent hydrolysis of nitrile of α -chloro- β -phenylpropionic acid. Starting from the $\alpha,\alpha,\alpha,\omega$ -tetrachloroalkane mentioned, the following scheme is valid for the synthesis of the α -amino acids (phenylalanine, p-chlorophenylalanine, glutamic acid, α -amino-adipic acid, α -aminopimelic acid, α -aminosuberic acid, and lysine) contained in this work, which appear in nature:



Card 2/3

$n = 0, 1, 2, \dots$; $\text{X} = \text{C}_6\text{H}_5, \text{ClC}_6\text{H}_4, \text{COOH}, \text{C}_2\text{H}_2\text{COOH}, \text{C}_6\text{H}_4(\text{CO})_2\text{N}$

Synthesis of D,L- α -aminocarboxylic Acids From
Compounds Containing the $\text{CCl}_2=\text{CH}$ Group

SOV/62-59-5-10/40

It was also shown that the synthesis of α -chloro- β -phenylpropionic acid can be carried out by the effect of chlorine on 1,1-dichloro-3-phenylpropene-1 in a formic acid medium with a yield of 63% of the theoretical yield, that is, without addition of mercury salts if anhydrous formic acid is used. There are 19 references, 10 of which are Soviet.

ASSOCIATION: Institut elementoorganicheskikh soedineniy Akademii nauk SSSR
(Institute of Elemental-Organic Compounds of the Academy of Sciences, USSR)

SUBMITTED: August 2, 1957

Card 3/3

5 (3)

AUTHORS:

Nesmeyanov, A. N., Freydlina, R. Kh.,
Belyavskiy, A. B.

SOV/62-59-6-12/36

TITLE:

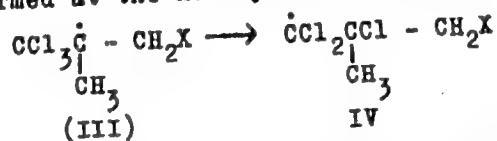
Hetero- and Homolytical Rearrangements in the Chemical Transformation of 1,1,1-Trichloro-2-methylpropene (Getero- i gomoliticheskiye peregruppirovki pri khimicheskikh prevrashcheniyakh 1,1,1-trikhlor-2-metilpropena)

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 6, pp 1028 - 1033 (USSR)

ABSTRACT:

The addition of HBr to 1,1,1-trichloro-2-methylpropene in the presence of benzoyl peroxide was investigated. Two isomers are formed at the homolytical affiliation:

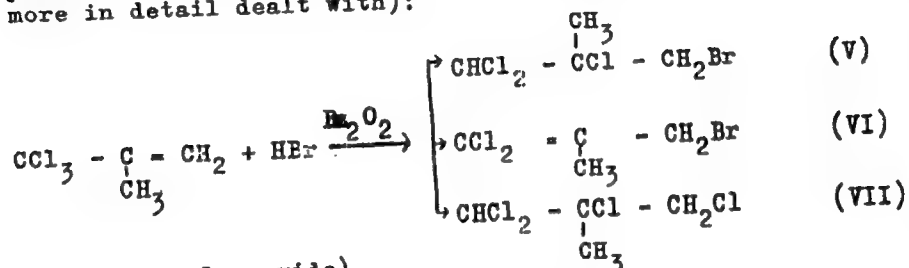


In the case of the electrophilic affiliation in an acetic acid medium an affiliation must have occurred because of the strongly inducing effect of the CCl_3 -group though this is in contra-

Card 1/3

Hetero- and Homolytical Rearrangements in the Chemical Transformation of 1,1,1-Trichloro-2-methylpropene SOV/62-59-6-12/36

diction to Markovnikov's rule. When heated, the affiliation yielded the following products (the formation scheme is still more in detail dealt with):



(Bz = benzoylperoxide)

The substances produced were identified by determining their melting point. 1,1,1-Trichloro-2-methylpropene reacts with benzene, toluene, and nucleophilic reagents with an allyl rearrangement. In the experimental part the different reactions are described in detail. There are 6 references, 5 of which are Soviet.

Card 2/3

Hetero- and Homolytical Rearrangements in the Chemical SOV/62-59-6-12/36
Transformation of 1,1,1-Trichloro-2-methylpropene

ASSOCIATION: Institut elementoorganicheskikh soedineniy Akademii nauk SSSR
(Institute of Elemental Organic Compounds of the Academy of
Sciences, USSR)

SUBMITTED: September 30, 1957

Card 3/3

5 (3)

AUTHORS:

Freydlina, R. Kh., Velichko, F. K.

SOV/62-59-7-11/38

TITLE:

Some Reactions of the Trichloromethyl- and ~~Di~~-Dichloroalkyl Compounds of Mercury (Nekotoryye reaktsii trikhlorometil'nykh i ~~Di~~-dikhloralil'nykh soedineniy rtuti)

PERIODICAL:

Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, 1959, Nr 7, pp 1225-1230 (USSR)

ABSTRACT:

In pursuance of previous reactions already known from publications concerning the compounds mentioned in the title (Refs 1-11) the behavior of the mercury salts of trichloromethyl was investigated with alkaline compounds: NaOH, NaOC₂H₅, the acid HCN and the neutral compounds KCN and KJ; moreover, with cadmium amalgam and alkylating and arylating agents. The following facts were revealed by these investigations: all trichloromethyl compounds of mercury react with hydrocyanic acid and with the above mentioned neutral compounds as inorganic mercury salts. The reaction with alkaline compounds gives the typical mercury organic compounds: with the reagent of Grignard both salts and mercury organic compounds are formed. Sodium amalgam with bromotrichloro methane yields the mercury dichloromethyl bromide.

Card 1/2

Some Reactions of the Trichloromethyl- and γ -Dichloro- SOV/62-59-7-11/38
alkyl Compounds of Mercury

1,1-dichloro-3-iodomercury-2-methyl-propene was obtained from 1,1-dichloro-3-iodo-2-methylpropene-1. The chemical properties of these compounds were determined. In the experimental part the different reactions, the preparation of the single substances and the reactions investigated are described. There are 18 references, 7 of which are Soviet.

ASSOCIATION: Institut elementoorganicheskikh soedineniy Akademii nauk SSSR
(Institute of Elemental Organic Compounds of the Academy of Sciences, USSR)

SUBMITTED: December 12, 1957

Card 2/2

5.3600

77066
SOV/62-59-12-10/43

AUTHORS: Kost, V. N., Sidorova, T. T., Freydlina, R. Kh.,
Nesmeyanov, A. N.

TITLE: Synthesis of α -Chlorocarboxylic Acids by Addition of
Chlorine in Formic Acid to Compounds Containing the
 $Cl_2C=CH$ -Group

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh
nauk, 1959, Nr 12, pp 2122-2125 (USSR)

ABSTRACT: The reaction

$$X(CH_2)_nCH=CCl_2 + Cl_2 \xrightarrow{HCOOH} [X(CH_2)_nCHClCCl_2OCH] \xrightarrow{H_2O} X(CH_2)_nCHClCOOH.$$

is conducted by gradually passing chlorine through a
solution of appropriate chloroolefin at 30° . The follow-
ing acids were prepared in this manner: α, β -dichloro-
propionic acid; α -chloro- β -methoxypropionic acid;
 α -chloro- β -formoxypropionic acid, yield 73%, mp $66-67^\circ$
(from benzene); α -chloro- δ -formoxyvaleric acid, yield

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Synthesis of α -Chlorocarboxylic Acids
by Addition of Chlorine in Formic Acid
to Compounds Containing the $\text{Cl}_2\text{C}=\text{CH}-$
Group

77066
SOV/62-59-12-10/43

82%, bp 138° (1.5 mm), n_D^{20} 1.4671; α, δ -dichlorovaleric
acid, α, ω -dichloroanthic acid; and α, ω -dichloro-
nonanoic acid, yield 71%, bp $142-143^\circ$ (0.5 mm),
 n_D^{20} 1.4768. There are 8 Soviet references.

ASSOCIATION: Institute of Element-Organic Compounds, Academy of
Sciences, USSR. (Institut elementoorganicheskikh
soyedineniy Akademii nauk SSSR)

SUBMITTED: March 25, 1958

Card 2/2

5 (3)

AUTHORS:

Nesmeyanov, A. N., Academician,
Karapetyan, Sh. A., Vasil'yeva, Ye. I., Freydlina, R. Kh.,
Corresponding Member AS USSR

SOV/20-127-2-30/70

TITLE:

Separation and Properties of Higher $\alpha, \alpha, \alpha, \omega$ -Tetrachloro Alkanes

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 127, Nr 2, pp 345-347 (USSR)

ABSTRACT:

Telomer mixtures are formed in the ethylene telomerization with CCl_4 from which the substances mentioned in the title were isolated and described in individual form. They contain up to 15 carbon atoms (Refs 1-3). The authors investigated the conditions of the vacuum rectification of these substances at a pressure of 0.2-0.5 mm and obtained pure telomers which have up to 23 C-atoms in one molecule. The rectification column used for this purpose is described. The mentioned tetrachloro alkanes were obtained from a telomer mixture from the plant of the Kaluzhskiy kombinat sinteticheskikh i natural'nykh dushistykh veshchestv (Kaluga Kombinat of Synthetic and Natural Aromatics) (Ref 5). The pressure amounted to 150 atmospheres absolute pressure and the molar ratio between ethylene and CCl_4 was approximately 20 : 1.

Card 1/3

A technical telomer mixture always contains traces of metal

Separation and Properties of Higher $\alpha, \alpha, \alpha, \omega$ -Tetrachloro SOV/20-127-2-30/70
Alkanes

chlorides which accelerate the dehydrochlorination of tetrachloro alkanes, especially at 160° and higher temperatures (Ref 6). The calcined soda (5%) added during the distillation transforms the metal chlorides into less active basic salts. This reduces rapidly the catalytic decomposition of the tetrachloro alkanes. The isolation of telomers above C₁₅ is difficult even with an

addition of soda. Therefore the tetrachloro alkanes were extracted by ethyl alcohol and acetone under utilization of their different solubility in organic solvents (Ref 2) after C₅ - C₉ had been

distilled off. They contained the telomers C₁₇ and C₂₅. Sub-

stances isolated in the first rectification were a second time distilled off on the same column in order to obtain the individual telomers (Table 1). Figure 1 shows the rules governing the changes of boiling temperature for the entire series of tetrachloro alkanes from C₅ - C₂₃. Figure 2 gives in a diagram the dependence of the densities and the molar volumes on the molecular weight of these substances. The molar volumes of the mixtures of tetrachloro alkanes are additive within a wide range. Their

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Separation and Properties of Higher $\alpha, \alpha, \alpha, \omega$ -Tetrachloro SOV/20-127-2-30/70
Alkanes

viscosity was determined only for lower telomers (Ref 7)
(Table 1, Fig 3 - determinations of L. M. Shulov). Yu. P.
Chizhov carried out the fractionated distillation (Fig 4) in the
determination of the physical constants (Table 1). There are
4 figures, 2 tables, and 8 references, 6 of which are Soviet.

ASSOCIATION: Institut elementoorganicheskikh soedineniy Akademii nauk SSSR
(Institute of Elemental Organic Compounds of the Academy of
Sciences, USSR)

SUBMITTED: May 9, 1959

Card 3/3

5 (3) .
AUTHORS:

Freydlina, R. Kh., Corresponding
Member AS USSR, Chukovskaya, Ye. Ts., Tsao I

SOV/20-127-2-32/70

TITLE:

Addition of Silanes to Unsaturated Compounds in the Presence of
Iron Pentacarbonyl

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 127, Nr 2, PP 352-355 (USSR)

ABSTRACT:

The authors described together with A. N. Nesmeyanov. (Ref 1) that the olefines enter into the reaction of thermal telomerization with different silanes (see Scheme). The use of this reaction is restricted to the decomposition of the olefines containing functional substituents, whereas the α -olefines polymerize under the hard conditions of the telomerization. Therefore a catalyst should be found which reduces the reaction temperature. Several of the 33 investigated substances were inactive (the ones crossed out, Table 1). This shows that many compounds catalyze the reaction between the olefines and silanes. The reaction leads, however, to the formation of a telomer-homologous mixture only in the presence of $TiCl_4$, or only an addition takes place (Table 2). In all other cases only an addition took place (Table 2). Iron pentacarbonyl was the most interesting one of these catalysts.

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Addition of Silanes to Unsaturated Compounds in the
Presence of Iron Pentacarbonyl

S07/20-127-2-32/70

In the presence of the latter the mentioned reactions proceed at 100-140°. SiCl_4 and methoxy trichlorosilane are an exception,

they are not added to ethylene. The reactions of ethylene with methyl dichlorosilane, triethoxysilane and triethylsilane, furthermore of propylene with methyl-dichlorosilane, and of vinyl ethyl ether with triethylsilane give in the presence of $\text{Fe}(\text{CO})_5$ yields of 60-85 % of the theoretically possible yield.

The reactions of the triethyl- and of the triethoxysilanes with ethylene in the presence of radical initiators as well as in the heating up to 250-300° are known to proceed either not at all or to lead to a small yield of the addition product (Ref 5). The process of the reaction between triethylsilane and vinyl ethyl ether in the presence of $\text{Fe}(\text{CO})_5$ was very interesting. It

yielded as main product apparently β -ethoxy-vinyl-triethyl-silane the structure of which was confirmed by the infrared spectrum. Reference 6 reports on the formation of an unsaturated by-product $\text{C}_6\text{H}_5\text{CH}=\text{CHSO}_3\text{Na}$ in the case of the homolytic addition of NaHSO_3 to styrene. Apparently an analogous reaction proceeds in the case

Card 2/3

Addition of Silanes to Unsaturated Compounds in the
Presence of Iron Pentacarbonyl

SOV/20-127-2-32/70

described here. The radical character of the reactions proceeding in the presence of $\text{Fe}(\text{CO})_5$ is also confirmed by the separation of by-products: the symmetrical hexaethyl- and hexamethoxy disilyl ethanes in the reaction of ethylene with triethyl- and triethoxy-silanes. This is possible almost only according to a homolytic scheme. The second possibility would be the reaction of ethylene with hexaethyl disilane (Refs 7, 8) (see Schemes). The authors proved, however, that hexaethyl disilane does not react with ethylene under the conditions of the mentioned reaction. Thus none of the two schemes holds in this case. A symmetrical product was observed in the homolytic telomerization of ethylene with H_2S (Ref 9). There are 2 tables and 10 references, 3 of which are Soviet.

ASSOCIATION: Institut elementoorganicheskikh soedineniy Akademii nauk SSSR
(Institute of Elemental Organic Compounds of the Academy of
Sciences, USSR)

SUBMITTED: April 16, 1959
Card 3/3

5(3)

AUTHORS:

SOV/20-127-3-26/71

Nesmeyanov, A. N., Academician, Freydlina, R. Kh., Corresponding Member, AS USSR, Petrova, R. G., Terent'yev, A. B.

TITLE:

Reaction Between 1,1,1-Trichloropropene and Mercaptans

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 127, Nr 3, pp 575 - 577 (USSR)

ABSTRACT:

At least 3 types of addition reactions (Ref 1) are known for 1,1,1-trichloropropene: a) electrophilic addition (of hypobromous acid, for example; this reaction takes place in contrast to the Markovnikov law); b) nucleophilic addition, occurring together with a re-arrangement of allyl, and finally c) radical addition; this takes place together with a re-arrangement of the meanwhile developed radicals, from type "A" to type "B" (see Scheme). The addition of thiophenol and benzyl mercaptan was investigated in the present work by means of 1,1,1-trichloropropene. 2,3,3-trichloropropylphenylsulphide (see Scheme) developed by means of an addition of the first mentioned substance (and an exposure to the light of a 100 w bulb). Its structure was determined in two ways (Ref 2). Thus the reaction takes place under the given con-

Card 1/3

Reaction Between 1,1,1-Trichloropropene and
Mercaptans

SOV/20-127-3-26/71

ditions, according to the homolytical mechanism. In the case of benzylmercaptan, however, 2 products develop: 2,3,3-trichloropropylbenzylsulphide (II) and 3,3-dichloropropene-2-yl-benzylsulphide (III). The latter compound is predominating. From the determination of the structure of the sulphides (II) and (III) by means of a different synthesis, it was found that HCl is separated during the reaction. Its amount corresponds to that of the produced sulphide (III) (see Scheme). The formation of sulphide (III) according to the method of a nucleophilic addition is less probable. 3,3,3-trichloropropylphenylsulphide developed during the reaction of 1,1,1-trichloropropene with thiophenol in the presence of sulphur as inhibitor of radical processes. Its structure was confirmed by the lacking of frequencies in the i.-r.-spectrum which are characteristic of the methyl group. There are 2 references, 1 of which is Soviet.

Card 2/3

Reaction Between 1,1,1-Trichloropropene and
Mercaptans

SOV/20-127-3-26/71

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk
SSSR (Institute for Elemental-organic Compounds of the Academy of Sciences, USSR)

SUBMITTED: May 6, 1959

Card 3/3

5(3)

AUTHORS:

Freydlina, R. Kh., Corresponding
Member of the Academy of Sciences, USSR,
Belyavskiy, A. B.

SOV/20-127-5-26/58

TITLE:

Telomerization of Ethylene With Carbon Tetrachloride,
Chloroform, and Ethyl Trichloroacetate in the Presence
of Iron Pentacarbonyl

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 127, Nr 5, pp 1027-1028
(USSR)

ABSTRACT:

As was proved by the authors (together with A. N. Nesmeyanov and Ye. Ts. Chukovskaya, Ref 1) iron pentacarbonyl initiates the addition reaction of the silanes to olefins. By basing the investigation on the homolytic character of this reaction the authors wanted to prove this property of $\text{Fe}(\text{CO})_5$ in the reaction mentioned in the title. It was found that this reaction takes place smoothly at 100 - 130° and under a pressure of 150 - 200 atm. In the case of CCl_4 $\alpha, \alpha, \alpha, \omega$ -tetrachloro alkanes and in the case of chloroform α, α, α -trichloro alkanes are formed. The reaction of the polychloromethanes and the yields in the individual telomer homologues are similar under similar conditions, utilization of $\text{Fe}(\text{CO})_5$, and of benzoyl

Card 1/2

Telomerization of Ethylene With Carbon Tetrachloride, 30V/20-127-5-26/58
Chloroform, and Ethyl Trichloroacetate in the Presence
of Iron Pentacarbonyl

peroxide as initiator. In one of the patents the telomerization reaction of ethylene with trichloroacetic acid ethyl ester in the presence of benzoyl peroxide is mentioned. However, several data are lacking in this patent. The latter reaction takes place smoothly in the presence of $\text{Fe}(\text{CO})_5$. It may be recommended as a preparative production method of α, α, ω -trichloro carboxyl acids with an even number of carbon atoms in the molecule. In the reaction between ethylene and some other compounds a trichloro- or dichloromethyl group and a mobile hydrogen atom no positive results could be obtained. There are 2 Soviet references.

ASSOCIATION: Institut elementoorganicheskikh soyedineniy (Institute of Elemental-Organic Compounds)

SUBMITTED: April 2, 1959

Card 2/2

5 (2, 3)
AUTHORS:

Freydlina, R. Kh., Corresponding Member SOV/20.128-2-26/59
AS USSR, Kost, V. N., Khorlina, M. Ya., Nesmeyanov, A. N.,
Academician

TITLE:

Addition of Hydrogen Bromide to 1,1,1,2-Tetrachloropropene-2
and 1,1,2-Trichloropropene-2 in the Presence of Benzoyl Peroxide

PERIODICAL:

Doklady Akademii nauk SSSR, 1959, Vol 128, Nr 2, pp 316-319 (USSR)

ABSTRACT:

The authors investigated the above topic in continuation of their own previous papers (Refs 1, 2) as well as in cooperation with L. I. Zakharkin (Ref 3) and A. B. Belyavskiy (Ref 4) on rearrangements of free radicals. The interaction between HBr and the substance mentioned first in the title led to a mixture of products. 1,1,2,2-Tetrachloro-3-bromopropene (I) with a yield of approximately 30% was isolated from the latter in addition to other compounds (II) - (IV) (see Scheme). The existence of (I) and (II) shows that the addition proceeds here with a rearrangement of the type mentioned in references 1-4. The intermediate radicals are apparently comparatively little stable and decompose under separation of a chlorine atom. The yield of (I) is therefore low, and (II) - (IV) occur in the reaction products. With respect to its composition,

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Addition of Hydrogen Bromide to 1,1,1,2-Tetrachloro- 30V/20-128-2-26/59
propene-2 and 1,1,2-Trichloropropene-2 in the Presence of Benzoyl Peroxide

constants, and infrared spectrum, substance I is identical with the 1,1,2,2-tetrachloro-3-bromopropane produced by the authors according to another scheme (see there), it differs, however, from the 1,1,1,2-tetrachloro-3-bromopropane produced by the chlorination of the $\text{CCl}_2=\text{CH}-\text{CH}_2\text{Br}$ with respect to

constants and infrared spectrum. Ethyl cellosolve HCl is split off from substance I by treatment with alkalis, which results in the production of compound III. The latter was identified as hydrochloride of the diethyl-amine derivative $\text{CCl}_2=\text{CCl}-\text{CH}_2\text{N}(\text{C}_2\text{H}_5)_2 \cdot \text{HCl}$ (V). As far as constants and

infrared spectrum are concerned, compound II corresponds to 1,1,2,2,3-pentachloropropene. Trichlorobromopropene III together with diethyl-amine and thiourea yields derivatives which were identified as hydrochloride and picrate respectively. When reacting with Hg, substance III yielded the trichloroallyl-mercury bromide which was identical with that produced by the usual method (Ref 5). As to its properties, tetrachloropropene IV corresponds to the well-known 1,1,2,3-tetrachloropropene, and together with diethyl-amine it yields the corresponding

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Addition of Hydrogen Bromide to 1,1,1,2-Tetrachloro- SOV/20-128-2-26/59
propene-2 and 1,1,2-Trichloropropene-2 in the Presence of Benzoyl Peroxide

derivative V. The addition of HBr to 1,1,2-trichloropropene-2 proceeds without rearrangement under formation of 1,1,2-trichloro-3-bromopropane (see Scheme). This reaction course is apparently connected with a greater stability of the radical A produced as against the radical $\text{CHClCCl}_2\text{CH}_2\text{Br}$ which might be produced by a rearrangement. As to its constant composition, and infrared spectrum, substance VI, i.e. $\text{HCCl}_2 - \text{CHCl} - \text{CH}_2\text{Br}$, which was produced in the last-mentioned reaction, is identical with the 1,1,2-trichloro-3-bromopropane. The isothiourea derivative furthermore obtained as picrate is identical with the corresponding derivative synthesized from the well-known 1,1,2-trichloro-3-bromopropane. There are 8 references, 7 of which are Soviet.

SUBMITTED: June 5, 1959

Card 3/3

5.2620

78004
SOV/62-60-1-10/37

AUTHORS:

Freydlina, R. Kh., Brynina, E. M., Nesmeyanov, A. N.

TITLE:

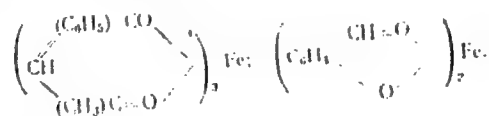
Metathetical Reactions of Iron Chelates

PERIODICAL:

Izvestiya Akademii nauk. Otdelenie khimicheskikh nauk, 1960, Nr 1, pp 59-62 (USSR)

ABSTRACT:

Iron triacetylacetonate undergoes a metathetical reaction with benzoylacetone and salicylaldehyde, forming the corresponding iron chelates:

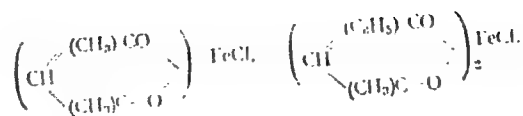


A reverse disproportionation takes place between ferrie chloride and iron triacetylacetonate or iron tribenzoylacetone (molar ratio 1:2), forming the corresponding monochloroderivatives of iron:

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Metathetical Reactions of Iron Chelates

73064
SOV/62-60-1-10/37



One chelate radical is replaced by chlorine in the reaction of iron triacetylacetonate and iron tribenzoylacetonate with acetyl chloride. There are 5 references, 3 Soviet, 1 U.S., 1 German. The U.S. reference is: U.S. patent 2659711, Nov. 17, 1953.

ASSOCIATION: Institute of Element-Organic Compounds, Academy of Sciences, USSR (Institut elementoorganicheskikh soyedinenii akademii nauk SSSR)

SUBMITTED: June 17, 1955

Card 2/2

81598

S/062/60/000/04/03/006
B004/B066

5.3700C

AUTHORS:

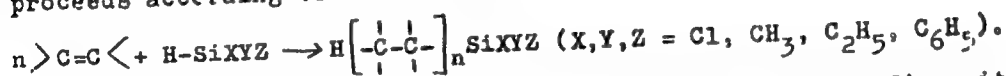
Freydlina, R. Kh., Chukovskaya, Ye. Ts., Karapetyan, Sh. A.,
Nesmeyanov, A. N.

TITLE:

Thermal Telomerization¹ of Olefins¹ With Silanes

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,
1960, No. 4, pp. 662 - 668

TEXT: In previous papers (Refs. 1 - 3) it was proved that olefins are thermally telomerized with compounds containing a Si-H bond. The reaction proceeds according to the scheme:



The first experiments were performed in steel autoclaves. Since it was supposed that the metallic walls act as catalyst, the experiments were repeated in sealed glass tubes at 320 - 340°C and 50 atm. As may be seen from the data in Table 1, the results were the same as in the steel autoclaves. The thermal telomerization thus takes place without initiators

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Thermal Telomerization of Olefins With
Silanes

81598
S/062/60/000/04/03/006
B004/B066

or catalysts but is initiated by dissociation of the silane at the Si-H bond. The present paper reports on the influence of temperature and ethylene concentration upon the telomerization of C_2H_4 with methyl-dichloro silane (Table 2, Fig. 1). The same laws hold as for the telomerization of C_2H_4 with CCl_4 and $CHCl_3$ (Refs. 4 - 6). With increasing C_2H_4

content of the initial mixture the amount of low-boiling telomers decreases, that of the higher-boiling increases, in which connection the content of each component passes a maximum. The data in Table 3 show that the reaction rate increases with increasing temperature. At 100 atm and 320 - 350°C a conversion of 60 - 80% is attained within 5 - 10 min. With rising temperature the content of low telomers decreases, that of higher telomers increases (Fig. 2). The experimental part describes the following reaction: 1) C_2H_4 with CH_3SiCl_2H . Methyl-ethyl-dichloro silane and methyl-n-butyl-dichloro silane were obtained. 2) C_2H_4 with $(C_6H_5)_3SiH$.

Triphenyl-ethyl-silane confirmed by infrared spectra and triphenyl-n-butyl-silane resulted, further a residue from $(C_6H_5)_3SiOSi(C_6H_5)_3$.

3) C_3H_6 with CH_3SiCl_2H in the presence of H_2PtCl_6 at room temperature.

Card 2/3

FREYDLINA, R.Kh.; PETROVA, R.G.; TERENT'YEV, A.B.

Synthesis and properties of polychlorodialkyl sulfides. Izv.
AN SSSR Otd.khim.nauk no.5:842-846 My '60. (MIRA 13:6)

1. Institut elementoorganicheskikh soyedineniy Akademii nauk
SSSR.

(Sulfides)

S/030/60/82697/000/007/006/011
B016/B058

5.3830
AUTHORS:

Freydlina, R. Kh., Corresponding Member of the AS USSR,
Vasil'yeva, Ye. I., Candidate of Chemical Sciences,
Karapetyan, Sh. A., Candidate of Technical Sciences

TITLE:

Telomerization Reaction and New Synthetic Materials

PERIODICAL:

Vestnik Akademii nauk SSSR, 1960, No. 7, pp. 49-57

TEXT: Soviet scientists have contributed much to the study of the telomerization reaction which is one of the production methods of new, highly synthetic materials. The USSR occupies a leading position in the use of this reaction for the purpose mentioned. The first industrial plant of the world is also being built here for this production. The authors call to mind the nature of the reaction mentioned. Such reactions can be initiated by radiation, radicals, or ions, the telomerization initiated by radicals being known best. The scheme

$XY + nCH_2=CH_2 \rightarrow X(CH_2CH_2)_nY$
telogen taxogen telomer

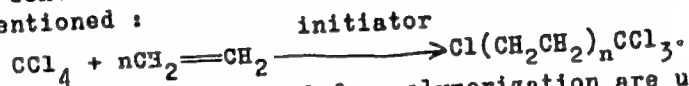
cannot reflect the whole complexity of the chain process under discussion. The authors describe the long

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chain of chemical conversions, and give an equation expressing all stages of the reaction mentioned :



As a rule, the same substances as used for polymerization are used to initiate telomerization, most frequently acyl- and alkyl-peroxides, azo compounds of the aliphatic series, organometallic compounds as well as ultraviolet light. The multitude of possibilities of synthesizing organic compounds by telomerization is further determined by the fact that various olefines, unsaturated compounds with functional groups, and various saturated compounds can be introduced into this reaction. The authors discuss the telomerization ability of individual compounds of the groups mentioned. All saturated compounds used for telomerization are joined by the authors into several types: 1) organic and inorganic halogen compounds; 2) organic compounds with an active hydrogen atom. The thoroughly investigated telomerization reactions with individual compounds are listed. Moreover, the use of telomers is discussed, and some problems of synthesis are mentioned, which can be solved by telomerization. The synthesis of mono-, di-, and polyfunctional compounds is

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explained next. The compounds synthesized from tetrachloro alkanes and their applications are listed in Table 1. A new industrial production method for Soviet synthetic fibers was elaborated by a team of several scientific institutions and industrial establishments under the guidance of A. N. Nesmeyanov. The following institutes contributed most: The Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR (Institute of Elemental-organic Compounds of the Academy of Sciences USSR), Gosudarstvennyy nauchno-issledovatel'skiy i proyektnyy institut azotnoy promyshlennosti i organicheskogo sinteza (State Scientific Research and Planning Institute of the Nitrogen Industry and Organic Synthesis) including its Dzerzhinsk Branch, and the Vsesoyuznyy nauchno-issledovatel'skiy institut iskusstvennogo volokna (All-Union Scientific Research Institute of Synthetic Fibers). Fig. 1 shows a scheme of a continuously operating apparatus for the production of tetrachloro alkane $\text{Cl}(\text{CH}_2\text{CH}_2)_n\text{CCl}_3$. Among the cellulose polymers, the manufacture of polyamides is gaining ever-increasing importance. Table 2 shows rules governing the change of the composition of telomers and Table 3 the properties of various fibers. The dependence of the content of tetrachloro alkane on the ethylene concentration may be seen from Fig. 2. There are 2 figures, 3 tables, and 5 Soviet

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Telomerization Reaction and New Synthetic
Materials

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B016/B058

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references.

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86410

S/062/60/000/008/018/033/XX
B013/B055

5.3700

2209, 1326, 1282

AUTHORS: Freydlina, R. Kh. and Kost, T. A.

TITLE: Effect of Nucleophilic Reagents on Compounds of the Type
 $[Cl(CH_2)_n CCl_2]_2$

PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk,
1960, No. 8, pp. 1387-1390

TEXT: The present paper treats the effect of nucleophilic reagents on compounds with the structure $[Cl(CH_2)_n CCl_2]_2$. These compounds are formed by direct catalytic hydrogenation of $\alpha, \alpha, \alpha, \omega$ -tetrachloro alkanes (Refs. 1, 2) or by the reaction of compounds of the type $[Cl(CH_2)_n CCl_2]_2$ with zinc. α, ω -disubstituted dichloro alkenes and monosubstituted trichloro alkenes were obtained. Contrary to saturated 1,3,3,4,4,6-hexachloro hexane and 1,1,1,3-tetrachloro propane, 1,3,4,6-tetrachloro 3-hexene enters into exchange reactions with nucleophilic reagents, however, not as easily as higher compounds of this type. 1,1,1,9-tetrachloro nonane was also dimerized by hydrogenation. Starting from 1,9,9,10,10,18-hexa-
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86 410

Effect of Nucleophilic Reagents on Compounds of the Type $[Cl(CH_2)_nCCl=]_2$ S/062/60/000/008/018/033/XX
B013/B055

chloro octadecane several compounds containing 18 or 20 carbon atoms in the chain were obtained: 1,9,10,18-tetrachloro 9-octadecene ($C_{18}H_{32}Cl_4$); 9,10-dichloro 9-octadecene 1,18-dicarboxylic acid ($C_{20}H_{32}Cl_2O_2$); 1-hydroxy-9,10,18-trichloro 9-octadecene ($C_{18}H_{33}Cl_3O$). The following compounds were prepared: 1,6-bisdiethylamino-3,4-dichloro hexene ($C_{14}H_{28}Cl_2N_2$); 1-acetoxy-3,4,6-trichloro 3-hexene ($C_8H_{11}Cl_3O_2$); 5,6-dichloro 5-decene 1,10-bisdiethyl-ammonium diiodide ($C_{22}H_{46}Cl_2I_2N_2$); 1,10-diethoxy-5,6-dichloro-5-decene ($C_{14}H_{26}Cl_2O_2$); 1-acetoxy-5,6,10-trichloro 5-decene ($C_{12}H_{19}Cl_3O_2$); 1,14-diethoxy-7,8-dichloro 7-tetradecene ($C_{18}H_{34}Cl_2O_2$), and 1,14-diethyl-amino-6,7-dichloro 7-tetradecene ($C_{22}H_{44}Cl_2N_2$). There are 5 Soviet references.

ASSOCIATION: Institut elementoorganicheskikh soedineniy Akademii nauk SSSR (Institute of Elemental Organic Compounds of the Academy of Sciences USSR)

SUBMITTED: February 17, 1959

Card 2/2

NESMEYANOV, A.N.; ^VFRIEDLINA, R.Kh.; SEMENOV, N.A.

Synthesis of dicarboxylic acids of the type $\text{HOOC}(\text{CH}_2)_m\text{C}_6\text{H}_4(\text{CH}_2)_n\text{COOH}$.
Izv. AN SSSR. Otd. khim. nauk no. 11: 1969-1973 N '60.

(MIRA 13:11)

1. Institut elementoorganicheskikh soedineniy AN SSSR.
(Acids, Organic)

80065

5.3700(B)(C)

S/020/60/132/01/39/064
B011/B126

AUTHORS: Freydlina, R. Kh., Corresponding Member of the AS USSR, Tsao I.,
Chukovskaya, Ye. Ts.

TITLE: The Interaction of Silicon Hydrides With Acrylonitrile in the
Presence of Iron Pentacarbonyl and Nickel Chloride

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 132, No. 1, pp. 49-152

TEXT: The authors studied the reaction of methyl-dichlorosilane and triethylsilane with acrylonitrile without admixtures or in the presence of iron pentacarbonyl and nickel chloride at 120-150°. It can be seen from the results obtained (Table 1) that the reaction does not take place without admixtures (Experiment No. 6). Neither is nickel chloride alone able to catalyze the reaction (Experiments No. 7 and 10). Triethylsilane does not react in the autoclave with acrylonitrile in the presence of iron pentacarbonyl (Experiment No. 13). Neither does methyl-dichlorosilane react with acrylonitrile in the presence of iron pentacarbonyl in a soldered-up glass ampoule (Experiment No. 9). However, this reaction does take place in the autoclave, and forms an adduct whose yield increases with the rise in the acrylonitrile excess (Experiments No. 1-5). The

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The Interaction of Silicon Hydrides With Acrylonitrile in the Presence of Iron Pentacarbonyl and Nickel Chloride

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authors suppose that the reaction only takes place when, apart from iron carbonyl, there are also impurities of heavy metal salts present. These salts form through the reaction of chlorosilane on the autoclave walls. Actually both methyl-dichlorosilane and triethylsilane add to acrylonitrile in the presence of small quantities of iron pentacarbonyl and nickel chloride (at the same time). These reactions take place just as well in the autoclave (Experiments No. 8 and 12) as in soldered-up glass ampoules (Experiment No. 11). Thus, α -methyl-dichlorosilylpropionitrile (in the case of methyl-dichlorosilane) or α -triethylsilylpropionitrile (in the case of triethylsilane) is formed. The mixed catalyst produced by the authors obviously catalyzes the ion mechanism of the reaction. The authors also quote: V. F. Mironov and G. I. Nikishin. They thank L. A. Leytes, Institut organicheskoy khimii AN SSSR (Institute of Organic Chemistry of the AS USSR) for taking and interpreting the spectra. There are 1 table and 14 references, 6 of which are Soviet.

ASSOCIATION: Institut elementoorganicheskikh sovedineniy Akademii Nauk SSSR
(Institute of Elemental-organic Compounds of the Academy of Sciences, USSR)

Card 2/3

80487

S/020/60/132/02/36/067
B011/B002

53700(B)

AUTHORS: Freydlina, R. Kh., Corresponding Member AS USSR, Chukovskaya,
Ye. Ts. Tsao-I, Nesmeyanov, A. N., Academician

TITLE: The Formation of Unsaturated Organosilicon Compounds During the
Interaction of Silicohydrides and Olefines in the Presence of
Iron Pentacarbonyl

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 132, No. 2, pp. 374-377

TEXT: The reaction between silicon hydrides and olefines in the presence of iron pentacarbonyl frequently takes place in two directions (Schemes (1) and (2)). An excess of silane however, proved to be favorable for the reaction course according to scheme (1), and develops $R'R''R'''SiCH_2CH_2R$, while an olefine excess develops $R'R''R'''SiCH=CHR$ (2). The direction of the reaction is influenced by another important factor, namely the structure of silicon hydride. Thus methyl-dichlorosilane favors the development of saturated reaction products, while triethyl silane is better suited for the development of unsaturated compounds. Thus, tetraethylsilane and a small amount of symmetric hexaethyl disilyl ethane develop during the reaction between triethyl silane

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The Formation of Unsaturated Organosilicon
Compounds During the Interaction of Silicohydrides
and Olefines in the Presence of Iron Pentacarbonyl

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S/020/60/132/02/36/067
B011/B002

and ethylene (molar ratio of 3:1). With a ratio of 1:5, triethyl vinyl silane develops. The authors investigated the reactions of methyl dichlorosilane and ethylene, propylene and decene-1. In the case of ethylene (Ref. 1), methyl-ethyl-dichlorosilane develops. With the molar ratios between 1:4 and 1:7, no vinyl-methyl-dichlorosilane developed. Mixtures of saturated and unsaturated products developed with the two other olefines. In the case of decene, the composition of the mixture consisting of unsaturated products (namely $\text{CH}_3\text{SiCl}_2\text{C}_{10}\text{H}_{19}$) and saturated ($\text{CH}_3\text{SiCl}_2\text{C}_{10}\text{H}_{21}$) is little changed if the ratio between silane and decene is kept between 1:2 and 5:1. The mixture of $\text{CH}_3\text{SiCl}_2\text{C}_3\text{H}_7$ (I) and $\text{CH}_3\text{SiCl}_2\text{C}_3\text{H}_5$ (II) developing from the reaction between methyl dichlorosilane and propylene (3:1), contains 75% of (I) and 25% of (II). If the ratio is 1:4, the mixture contains 24% of (I) and 76% of (II). Iron pentacarbonyl is the only catalyst of the above reaction, and acts without any cocatalysts. In reaction (2) decene acts as hydrogen acceptor and is thus hydrogenated into decane. The authors assume that a radical or cation of $\text{CH}_3\text{SiCl}_2\text{CH}_2\text{CHCH}_2\text{C}_7\text{H}_{15}$ (A) develops during the reaction, with o representing a

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The Formation of Unsaturated Organosilicon
Compounds During the Interaction of Silicohydrides
and Olefines in the Presence of Iron Pentacarbonyl

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B011/B002

positive charge or an unpaired electron. Particle A is hydrogenated during the interaction with silane, while it is dehydrogenated during the reaction with olefine (see a somewhat simplified scheme). Intensity and structure of the above substances were proven by Raman and IR-spectra (taken by L. A. Leytes). Fig. 1 shows the spectrum of (V) taken by the apparatus type IKS-14. V. F. Mironov, G. I. Nikishin are mentioned. There are 1 figure and 14 references, 13 of which are Soviet. ✓

ASSOCIATION: Institut elementoorganicheskikh soedineniy Akademii nauk SSSR
(Institute of Elemental-organic Compounds of the Academy of
Sciences, USSR)

SUBMITTED: February 5, 1960

Card 3/3

S/020/60/132/03/32/066
B011/B008

5.3200
5.3600

AUTHORS: Kost, V. N., Sidorova, T. T., Freydlina, R. Kh.,
Corresponding Member AS USSR, Nesmeyanov, A. N., Academician

TITLE: Homolytic Addition of Hydrogen Bromide to 1-Fluoro-1,
1-Dichloropropene

PERIODICAL: Doklady Akademii nauk SSSR, 1960, Vol. 132, No. 3,
pp. 606-608

TEXT: The authors determined in their paper the divergent behavior of 1-fluoro-1, 1-dichloropropene in the reaction of the homolytic addition from that of 1,1,1-trichloropropene. Two fluoro-dichloro-bromopropanes were obtained as a consequence of the reaction of the 1-fluoro-1, 1-dichloropropene with HBr at an ultraviolet exposure: 1-fluoro-1, 1-dichloro-3-bromopropane and 1-fluoro-1,2-dichloro-3-bromopropane at a ratio 2:1. The reaction proceeded as chain reaction of free radicals. The addition of HBr to 1,1,1-trichloro-propene leads, under equal conditions, to a single product: 1,1,2-trichloro-3-bromopropane.

Card 1/2

Homolytic Addition of Hydrogen Bromide
to 1-Fluoro-1, 1-Dichloropropene

S/020/60/132/03/32/066
B011/B008

That means, the reaction takes its course under a regrouping in the free radical developing in the meantime (similar to the case of the initiation of the reaction by benzoyl peroxide, Ref. 4). The scheme (I) illustrates the reaction of the fluoro-dichloro-propene with HBr. Apparently, the rate of regrouping of the radical $\text{CH}_2\text{Br}\dot{\text{C}}\text{HCCl}_2\text{F}$ is reduced considerably due to the stabilizing action of the fluorine in it. Thus, this rate gets commensurable to that of this radical with HBr. This double mode of reaction of the free radical (with or without regrouping) is observed here for the first time. The authors proved the structure of the produced fluoro-dichloro-bromopropane on schemes (II) and (III) as well as by the production of the picrates and other reactions. There are 11 references, 9 of which are Soviet.

ASSOCIATION: Institut elementoorganicheskikh sovedineniy Akademii nauk
SSSR (Institute of Elemental Organic Compounds of the
Academy of Sciences, USSR)

SUBMITTED: February 24, 1960

Card 2/2

PHASE I BOOK EXPLOITATION

SOV/5630

Freydlina, Rakhil' Khatskelevna, Corresponding Member AS USSR, and Shavarsh Avetisovich Karapetyan

Telomerizatsiya i novyye sinteticheskiye materialy (Telomerization and New Synthetic Materials) Moscow, Izd-vo AN SSSR, 1961. 102 p. (Series: Akademiya nauk SSSR. Nauchno-populyarnaya seriya) 10,000 copies printed.

Ed. of Publishing House: O.M. Yenisherlova; Tech. Ed.: L.V. Yepifanova.

PURPOSE: This book is intended for the general reader interested in synthetic materials.

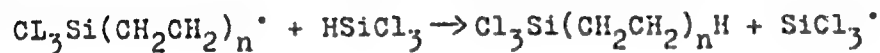
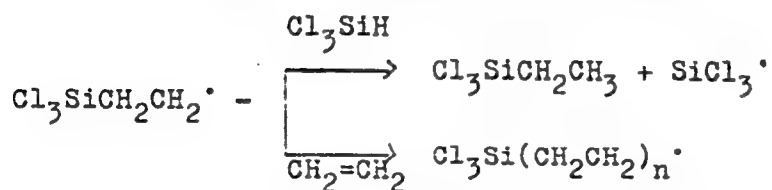
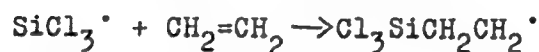
COVERAGE: The book describes a purportedly new method of producing synthetic materials with the aid of the telomerization reaction. The production and properties of enant fiber, which is superior to caprone and nylon in the authors' opinion, are described in detail. The reader is assumed to have a knowledge of chemistry through the high-school level. R. Kh. Freydlina wrote the section on telomerization and the chapter on telomer conversion. The authors thank G. L. Slonimskiy and T. I. Sheyn. There are 7 references, all Soviet.

Card ~~1/3~~

Thermal telomerization ...

S/561/61/000/006/012/081
D205/D302

suggests that the telomerization is initiated by the dissociation of the Si-H bond and proceeds according to




Card 2/5

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Thermal telomerization ...

S/661/61/000/006/012/081
D225/D302

Thermal telomerization gives higher conversions than that initiated chemically by azo-bis-iso-butyronitrile or benzoyl peroxide. The structure of the addition product of methyl dichlorosilane to propylene was investigated by spectroscopic methods showing that no iso-propyl methyl silane was formed. The influence of temperature, pressure and ethylene concentration in the thermal telomerization of ethylene with methyl dichlorosilane was studied. With the increase of ethylene concentration the content of the higher telomers increases. The velocity of the reaction is strongly accelerated by the temperature rise. At 150 atm. and 320 - 350°C, 60 - 80% are converted in 5 - 10 minutes. The temperature rise effects also the composition increasing the content of the lower telomers in the reaction mixture. However, application of thermal telomerization is limited by the decomposition of unsaturated compounds in the reaction conditions. Therefore, a series of catalysts was tried in the reaction: HSbCl_5 , $\text{H}_2\text{SnCl}_6 \cdot 6\text{H}_2\text{O}$, $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ and also TiCl_4 and ZrCl_4 . In the presence of H_2PtCl_6 the reaction with ethylene and



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Thermal telomerization ...

S/661/61/000/006/012/081
D225/D302

propylene takes place at room temperature giving only addition products. In the presence of $ZrCl_4$ the reaction between methyl dichlorosilane and ethylene proceeds at $175 - 180^\circ C$ yielding 80 - 90% of methyl ethyl dichlorosilane. In the presence of $H_2SnCl_6 \cdot 6H_2O$ or $TiCl_4$, ethylene and methyl dichlorosilane enter the telomerization reaction at $200 - 220^\circ C$ giving telomers having 1,3 (CH_2CH_2) groups and which are identical with those obtained in the thermal telomerization. A. L. Klebanskiy (VNIISK, Leningrad), V. S. Chugunov, D. N. Andreyev and M. G. Voronkov (IKhS AN SSSR, Leningrad), S. N. Borisov (VNIISK, Leningrad), G. I. Nikishin (IOKh AN SSSR, Moscow), V. O. Reykhsfel'd (LKhTI, Leningrad), V. P. Mironiv, (IOKh AN SSSR, Moscow), S. A. Golubtsov (Moscow) and V. A. Ponomarenko (IOKh AN SSSR, Moscow) took part in the discussion. There are 2 figures, 4 tables and 15 references: 12 Soviet-bloc and 3 non-Soviet-bloc. The references to the English-language publications read as follows: S. Nozakura and S. Konotsune, Bull. Chem. Soc. Japan., 29, 322, 326 (1957); S. Nozakura, Bull. Chem. Soc. Japan, ✓

Card 4/5

Thermal telomerization ...

S/661/61/000/006/012/081
D205/D302

29, 660, 784, (1957); J. L. Speier, J. A. Webster and G. H. Barnes, J. Amer. Chem. Soc., 79, 974, (1957).

ASSOCIATION: Institut elementoorganicheskikh soyedineniy Akademii nauk SSSR, Moscow (Institute of Elemental Organic Compounds, Academy of Sciences USSR, Moscow)

Card 5/5 .

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FREYDLINA, R.Kh.; VELICHKO, F.K.

Synthesis and chemical properties of β -haloallyl compounds
of mercury. Izv. AN SSSR. Otd. khim. nauk no. 1:55-60 Ja '61.
(MIRA 14:2)

1. Institut elementoorganicheskikh soyedineniy AN SSSR.
(Mercury organic compounds)

S/081/62/000/014/009/039
B166/B144

AUTHORS: Nesmeyanov, A. N., Freydlina, R. Kh., Kost, V. N.,
Khorlina, M. Ya., Sidorova, T. T., Petrova, R. G.,
Terent'yev, A. B.

TITLE: Connection between the structure of polyalkylhalide radicals
and their ability to regroup in solution

PERIODICAL: Referativnyy zhurnal. Khimiya, no. 14, 1962, 178, abstract
14Zh41 (Tr. po khimii i khim. tekhnol. [Gor'kiy], no. I,
1961, 106-115)

TEXT: A review of the authors' work on the homolytic addition of HBr, CCl_3 , Br, Br_2 , $\text{C}_6\text{H}_5\text{SH}$ and $\text{C}_6\text{H}_5\text{CH}_2\text{SH}$ to olefins $\text{XCCl}_2\text{CY} = \text{CH}_2$ (I), where
 $\text{X} = \text{Cl}, \text{F}, \text{H}, \text{CH}_3$ and $\text{Y} = \text{H}, \text{Cl}, \text{Br}, \text{CH}_3$. The results of the work show
that the aforesaid reactions proceed according to the general scheme:
 $\text{I} + \text{HBr} \rightarrow \text{HCclXCYclCH}_2\text{Br} + \text{CClX} = \text{CYCH}_2\text{Br} + \text{HCclXCYclCH}_2\text{Cl}$. This
indicates that the initially formed polyalkylhalide radicals (PR) are

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Connection between the structure ...

S/081/62/000/014/009/039
B166/B144

rearranged and then stabilized either by adding an H or by dehalogenation; moreover the latter leads to the chain of reaction being continued. The exception is compounds with $X = F$, which along with rearranged products also give products which are not rearranged. It was found that the rearrangement of PR tends towards the formation of more stable radicals. A table of the relative stability of the PR is drawn up:

$\dot{C}Cl_2CHClCH_2X > CCl_3\dot{C}HCH_2X$ (when $X = Br, Cl, CCl_3, C_6H_5$);
 $\dot{C}Cl_2CCl(CH_3)CH_2Br > CCl_3\dot{C}(CH_3)CH_2Br$; $\dot{C}Cl_2CCl_2CH_2Br > CCl_3\dot{C}ClCH_2Br$;
 $\dot{C}HClCHClCH_2Br > CHCl_2\dot{C}HCH_2Br$; $CHCl_2\dot{C}ClCH_2Br > \dot{C}HClCCl_2CH_2Br$;
 $CH_3\dot{C}ClCHClCH_2Br > CH_3CCl_2\dot{C}HCH_2Br$; $CFCl_2\dot{C}HCH_2Br \approx CFClCHClCH_2Br$;
 $\dot{C}FClCBrcClCH_2Br \approx CFCl_2\dot{C}BrCH_2Br$. 15 references. [Abstracter's note:
 Complete translation.]

✓

Card 2/2

FRYDLINA, L.L.N.; LOPYLOVA, N.V.

Identification of $\sigma, \alpha, \alpha, \omega$ -tetrachloro alkanes and α, β -unsaturated α, α, ω -trichloro alkenes with the use of picrates and their isothiuronium derivatives. Izv. AN SSSR. Otd. khim. tekhn. 1:172-174 Jan 1961. (CIA A 14:2)

1. Institut elementoorganicheskikh soedineniy AN SSSR.
(Isothiuronium compounds) (Paraffins) (Olefins)
(Picric acid)

FREYDLINA, R.Mh.; BELYAVSKIY, A.B.

Telomerization of ethylene and carbon tetrachloride or
chloroform in the presence of chromium, molybdenum, and tungsten
carbonyls. Izv. AN SSSR. Otd. Khim. nauk no. 1:177-178 Ja '61.
(MIRA 14:2)

1. Institut elementoorganicheskikh soyedineniy AN SSSR.
(Ethylene) (Carbon tetrachloride) (Carbonyls)

22516

5.3700 2209

S/062/61/000/004/005/008
B118/B208

AUTHORS: Braynina, E. M., Freydlina, R. Kh., and Nesmeyanov, A. N.
TITLE: A new method of synthesizing zirconium tetraacyloxy derivatives
PERIODICAL: Izvestiya Akademii nauk SSSR. Otdeleniye khimicheskikh nauk, no. 4, 1961, 608-612

TEXT: The authors of the present paper studied the synthesis of zirconium tetraacyloxy derivatives by allowing zirconium tetraacetyl acetate to react with aliphatic carboxylic acids. Organic acids were found to react when heated with zirconium tetraacetyl acetate, and to give neutral salts, separating acetyl acetone, according to the equation
$$(C_5H_7O_2)_4Zr + RCOOH \longrightarrow (RCOO)_4Zr + C_5H_8O_2$$

This reaction gives a quantitative yield of the end product after 3-8 hr. The reactions of zirconium tetraacetyl acetate with valerianic, capronic, and enanthic acid were performed in the stream of dry nitrogen, by using these acids in excess. Liquid products were obtained which crystallized when stored, but

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A new method of synthesizing...

partially decomposed with high-vacuum distillation. Zirconium tetraacetyl acetate reacted with ω -chloro-undecanoic, lauric, palmitic, and stearic acid in a molar ratio of 1 : 4 of the components, in benzene or octane solution. Zirconium tetrapalmitate and zirconium tetrastearate resulted in the form of light powders. They partially decomposed on recrystallization. The advantage of this method is that the products separated from the reaction mixture are analytically pure without further purification. This was confirmed by tests for C, H, Zr, Cl. Substitution of acyloxy groups for the acetyl acetate groups also takes place in the respective manganese and cobalt compounds. Reaction of manganese triacetyl acetate and cobalt triacetyl acetate with palmitic and stearic acid yielded manganese dipalmitate, manganese distearate, and cobalt distearate. The latter could also be obtained by reacting cobalt diacetyl acetate with stearic acid in a dry nitrogen stream. There are 17 references: 3 Soviet-bloc and 14 non-Soviet-bloc. The three references to English-language publications read as follows: R. N. Kapoor, R. C. Mehrotra, Chem. Industr. 68 (1958); R. N. Kapoor, R. C. Mehrotra, J. Chem. Soc. 422 (1959); S. Prasad, V. Rama Reddy, J. Indian Chem. Soc. 35, 907 (1958).

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